MEJORA DE LA EFICIENCIA DE CONVERSIÓN DE ENERGÍA FOTOVOLTAICA EMPLEANDO ELECTRODOS BASADOS EN NANOTUBOS DE TIO<sub>2</sub> DOPADOS CON BORO Y SENSIBILIZADOS CON PUNTOS CUÁNTICOS DE CALCOGENUROS DE CADMIO

## ANDRÉS FABIÁN GUALDRÓN REYES

UNIVERSIDAD INDUSTRIAL DE SANTANDER FACULTAD DE CIENCIAS ESCUELA DE QUÍMICA DOCTORADO EN QUÍMICA BUCARAMANGA 2018 MEJORA DE LA EFICIENCIA DE CONVERSIÓN DE ENERGÍA FOTOVOLTAICA EMPLEANDO ELECTRODOS BASADOS EN NANOTUBOS DE TIO<sub>2</sub> DOPADOS CON BORO Y SENSIBILIZADOS CON PUNTOS CUÁNTICOS DE CALCOGENUROS DE CADMIO

ANDRÉS FABIÁN GUALDRÓN REYES

Tesis doctoral presentada como requisito para optar al título de Doctor en Química

Directores

MARTHA EUGENIA NIÑO GÓMEZ Doctora en Química

ANGEL MANUEL MELÉNDEZ REYES Doctor en Química

UNIVERSIDAD INDUSTRIAL DE SANTANDER FACULTAD DE CIENCIAS ESCUELA DE QUÍMICA DOCTORADO EN QUÍMICA BUCARAMANGA 2018

## IMPROVEMENT OF PHOTOVOLTAIC CONVERSION EFFICIENCY BY USING CADMIUM CHALCOGENIDES QUANTUM DOT-SENSITIZED BORON DOPED TiO<sub>2</sub> NANOTUBES BASED ELECTRODES

## ANDRÉS FABIÁN GUALDRÓN REYES

Doctoral thesis presented as a requirement to aim for the degree of Doctor in Chemistry

supervisors:

MARTHA EUGENIA NIÑO GÓMEZ Doctor in Chemistry

ANGEL MANUEL MELÉNDEZ REYES Doctor in Chemistry

UNIVERSIDAD INDUSTRIAL DE SANTANDER FACULTAD DE CIENCIAS ESCUELA DE QUÍMICA DOCTORADO EN QUÍMICA BUCARAMANGA 2018 For my parents and my sister, Norma, Venancio and Daniela. For my best friends, soul brothers: Jerffersson and Fernando. For my partner in the life: Edna. Your eyes, my road...

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#### RESUMEN

TÍTULO: MEJORA DE LA EFICIENCIA DE CONVERSIÓN DE ENERGÍA FOTOVOLTAICA EMPLEANDO ELECTRODOS BASADOS EN NANOTUBOS DE TIO<sub>2</sub> DOPADOS CON BORO Y SENSIBILIZADOS CON PUNTOS CUÁNTICOS DE CALCOGENUROS DE CADMIO\*

AUTOR: ANDRÉS FABIÁN GUALDRÓN REYES.\*\*

**PALABRAS CLAVES:** Nanotubos de TiO<sub>2</sub>, tri-dopaje de B,N,F, sensibilización por puntos cuánticos, calcogenuros de cadmio, efecto sinérgico.

El desempeño fotovoltaico de una celda solar depende principalmente de la colección de luz y el transporte de portadores a través del dispositivo. En este sentido, con el fin de mejorar la eficiencia de conversión de energía (PCE) en celdas solares sensibilizadas por puntos cuánticos (QDSSCs) convencionales, se prepararon fotoánodos basados en nanotubos de TiO<sub>2</sub> tridopados con boro, nitrógeno y flúor (BNF-TNTs) y sensibilizados con puntos quánticos (QDs) de diferentes calcogenuros de cadmio como CdSe y heterouniones basadas en CdS/CdS<sub>1-x</sub>Se<sub>x</sub> y Mn-CdS/Bi<sub>2</sub>S<sub>3</sub>. Mediante la caracterización fisicoquímica, foto(electro)química y fotovoltaica de estos materiales, se pudo observar que el dopaje con boro y la sensibilización con los calcogenuros generan un efecto sinérgico, lo que mejoró la absorción de fotones de baja energía, e incrementó el número de electrones transportados hacia el colector de corriente. Esto generó una alta fotocorriente en el dispositivo, lo que derivó en una PCE de 2.58 %. Factores importantes como (1) la mejora de la transferencia electrónica desde una cantidad adecuada de niveles energéticos Ti<sup>3+</sup> hacia los calcogenuros, y (2) el balance entre el alineamiento de bordes de banda apropiado en la interfase BNF-TNTs/QDs y la habilidad de colección de luz por parte de los materiales compuestos, influenciaron directamente en el rendimiento fotovoltaico de las QDSSCs estudiadas.

<sup>\*</sup>Tesis doctoral

<sup>\*\*</sup>Facultad de Ciencias. Escuela de Química. Directores: Martha Eugenia Niño Gómez, Angel Manuel Meléndez Reyes.

#### ABSTRACT

**TÍTLE:** IMPROVEMENT OF PHOTOVOLTAIC CONVERSION EFFICIENCY BY USING CADMIUM CHALCOGENIDES QUANTUM DOT-SENSITIZED BORON DOPED TIO<sub>2</sub> NANOTUBES BASED ELECTRODES\*

AUTOR: ANDRÉS FABIÁN GUALDRÓN REYES.\*\*

**PALABRAS CLAVES:** TiO<sub>2</sub> nanotubes, B,N,F-tridoping, quantum dot sensitization, cadmiun chalcogenides, synergistic effect.

The photovoltaic performance of a solar cell depends mainly on the light harvesting and carrier transport abilities into a device. In this sense, with the aim to improve the photoconversion efficiency (PCE) in conventional quantum dot-sensitized solar cells (QDSSCs), boron, nitrogen and fluorine-tridoped TiO<sub>2</sub> nanotubes (BNF-TNTs) were prepared and sensitized with diverse cadmium chalcogenide quantum dots (QDs) like CdSe and CdS/CdS<sub>1-x</sub>Se<sub>x</sub> and Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> based heterojunctions. Through physicochemical, photo(electro)chemical and photovoltaic characterization of these materials, it was observed that B-doping and chalcogenide sensitization induced a synergistic effect, which enhanced the absorption of low-energy photons and increased the number of transported electrons to the current collector. This produced a high photocurrent in the device, achieving a PCE around 2.58 %. Main factors as (1) the improvement of electron transfer from an adequate Ti<sup>3+</sup> energy levels to chalcogenides, and (2) the balance between the suitable band alignment in the BNF-TNTs/QDs interface and the light harvesting ability of the composite materials influenced directly on the photovoltaic performance of the studied QDSSCs.

<sup>\*</sup>Doctoral thesis

<sup>\*\*</sup>Faculty of Science. Department of Chemistry. Supervisors: Martha Eugenia Niño Gómez, Angel Manuel Meléndez Reyes.

#### INTRODUCTION

The high consumption of conventional energy sources as carbon, crude oil and natural gas, has promoted a negative impact in the environment due mainly to the increase of CO<sub>2</sub> in the atmosphere. Thus, some "green" and more ecofriendly energy sources have been studied to decrease the use of non-renewable energy sources. The use of sunlight as an energy source has been the aim of research during recent years, carrying out the fabrication of photovoltaic devices as solar cells. Here, the sunlight can be harnessed, producing electricity. The photoconversion efficiency (PCE) of a dye-sensitized device depends mainly on the photoanode material, which absorbs the incident light and promotes charge carrier photogeneration (electrons). Carriers are transported through the solar cell, producing a photocurrent. The most efficient photovoltaic devices are composed by Si-based harvesters, reaching a PCE higher than 25%. Nonetheless, the Si processing and thereby, the solar cell fabrication increase the cost production. In this sense, consider the solar energy as an alternative energy source to replace the conventional ones is not profitable yet. To overcome this issue, other kind of low-cost materials as  $TiO_2$  have been studied in phovoltaics, due to their optical features, high chemical, thermal stability and low toxicity. Some nanostructured morphologies as nanoparticle films have been prepared and tested in optoelectronic devices. However, oriented structures as nanotubes can address electron transport to the current collector, enhancing the PCE of the cell.

Recent reports have shown the enhancement of PCE in photoanode composites into quantum dot-sensitized solar cells (QDSSCs), by varying experimental conditions as sensitizer concentration, deposition methods of chalcogenides, the device architecture, etc., to reach an actual record around 12 %. Nonetheless, the electronic conductor-sensitizer interaction has not been widely studied, which has led to propose hypothesis for achieving lower PCEs than 4 - 5 % for this kind of devices.

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The latter is the starting point to consider additional limitations into composites that decrease the overall PCE. Accordingly, a question must be answered: How do the photovoltaic properties of composites impact on the performance of QDSSCs to improve their PCE?

Herein, it is studied the visible-light harvesting and carrier transport abilities of cadmium chalcogenides quantum dots (QDs)-sensitized boron, nitrogen and fluorine-tridoped TiO<sub>2</sub> nanotubes (BNF-TNTs) based photoanodes. The aim of this work was threefold: study (1) the role of boron doping on the synergistic behaviour of CdSe QDs sensitized BNF-TNTs, (2) the influence of Cd-Cd energy levels into chalcogenide sensitizers, as CdS QDs and ternary CdS<sub>1-x</sub>Se<sub>x</sub>, on the carrier mobility into BNF-TNTs/CdS/CdS<sub>1-x</sub>Se<sub>x</sub> composites, and (3) to propose an alternative to improve the low PCEs of QDSSCs using low-band gap chalcogenides as Bi<sub>2</sub>S<sub>3</sub>, by the incorporation of Mn-doped CdS QDs as a carrier transport pathway. During the development of this work, the possible factors for obtaining a low photovoltaic performance in this type of devices are explained and supported with experimental evidence. Furthermore, some recommendations are given to consider in the preparation of photoanodes with enhanced light harvesting and carrier transportation features.

The enhancement of PCE in a QDSSC can be achieved to understand the factors affecting the photovoltaic properties of the composites. Considering that the electronic structure of chalcogenides QDs can be tuned during their synthesis, and BNF-TNTs shows a high electron donor states content, it is possible to improve the low-energy harvesting and carrier mobility pathway by establishing a synergistic behaviour and a suitable band edge alignment in the TiO<sub>2</sub>/sensitizer interface.

## **OBJECTIVES**

## 1.1. GENERAL OBJECTIVE

Enhance the PCE of a conventional QDSSC by using cadmium chalcogenide QDs-sensitized BNF-TNTs, establishing a synergistic effect between B-doping and chalcogenide sensitization.

### 1.2. SPECIFIC OBJECTIVES

- a) Determine the suitable amount of incorporated boron into photoactive BNF-TNTs.
- b) Study the influence of CdS/CdS<sub>1-x</sub>Se<sub>x</sub> heterojunction on the photo(electro)chemical and photovoltaic properties of sensitized BNF-TNTs composites.
- c) Correlate the calculated PCE of QDSSCs with the S/Se molar ratio of the CdS<sub>1-x</sub>Se<sub>x</sub> ternary alloy contained into composites.
- d) Predict the favourability of adding Mn-CdS QDs in the improvement of photovoltaic performance of Bi<sub>2</sub>S<sub>3</sub>-based QDSSCs, by using photo(electro)chemistry (additional).

#### 2. BACKGROUND

#### 2.1. Fundamentals of quantum dot-sensitized solar cells

After the fabrication of the first low-cost efficient dye-sensitized solar cell by O'Regan and Grätzel in 1991,<sup>1</sup> the light harvesting, and energy conversion efficiency of a photovoltaic device have been a hot topic in the actuality. The research of new materials with both enhanced low-energy absorption and carrier transport capabilities has been carried out to consider the preparation of third-generation solar cells, where narrow band gap based sensitizers are deposited on wide band gap semiconductor photoanodes as TiO<sub>2</sub> or ZnO.<sup>2</sup> Advantages as facile fabrication, multiple electron-hole pair generation during irradiation, high extinction coefficient and tunable band gap depending on nanoparticle size, have highlighted the cadmium chalcogenides in quantum-dot sensitized solar cells (QDSSCs), with an actual PCE higher than 11-12 %.3,4 These materials have facilitated a better understanding about the photovoltaic properties of more complex structures, for instance, electron separation and mobility mechanism into perovskite-based solar cells, which show the highest PCE record around 22 %.<sup>5</sup> Because of this, the number of publications ascend to more of 200 from 2013, reaching the highest peak of the investigation in this kind of devices around 275 in 2014.<sup>2</sup> Unfortunately, some main aspects of the QDSSCs as the stability of sensitizer, the band alignment into photoanode, the device architecture or the electrolyte nature have been mentioned as the possible issues for limiting the PCE.<sup>2,6–8</sup> This has also decreased the number of investigations in recent years. Nonetheless, many research groups around the world still propose alternatives to improve the PCE of QDSSCs to be competitive in the photovoltaic area as their analogous, silicon-based solar cells.

Concerning to the photoanode material used in QDSSCs, narrow-band gap chalcogenides-based sensitizer quantum dots (QDs) (for instance CdX; X= S, Se, Te; CuInS<sub>2</sub>, PbS, among others) are commonly deposited on wide band gap

semiconductors as TiO<sub>2</sub>.<sup>8–11</sup> The latter material acts as an electron conductor into the cell. Depending on the size of the QDs, the photoactivation energy of the sensitizer can be tuned to achieve two main requirements: (1) the improvement of the visible-light absorption to photogenerate more carriers and (2) the relative positions of valence and conduction band edges (VB and CB, respectively) to match with TiO<sub>2</sub> and facilitate carrier mobility (Figure 1).<sup>11</sup> Accordingly, when CB shows a higher energy value (in energy scale) than that of TiO<sub>2</sub>, photogenerated electrons can be injected to the latter semiconductor, flowing to the back contact. However, the unmatching of the CB in the TiO<sub>2</sub>/sensitizer interface can generate an unsuitable band alignment to electron transport, decreasing the PCE in the device.<sup>2,12</sup>

**Figure 1.** Schematic representation of  $E_g$  and band edge tuning in PbS QDs by varying their particle size.<sup>2,11,12</sup>



Another item to consider in the photoanode preparation is the morphology of the electron conductor. Many reports in photovoltaics have shown the use of TiO<sub>2</sub> nanoparticle films as support to chalcogenide deposition.<sup>3,7,8,13</sup> However, the nanoparticle interconnection into the film generates grain boundaries which act as electron recombination centers.<sup>13,14</sup> This could be another main cause to provide a

low PCE in the solar cells. Herein, oriented nanostructures are an alternative to address the electron flow through the photoanode, increasing the photocurrent in the system. Compared with a TiO<sub>2</sub> film, vertical TiO<sub>2</sub> nanotubes can achieve more deposited sensitizer along the tubular structure, assisting the light harvesting to produce more charge carriers.<sup>12,13,15</sup> Nanotube arrays are conventionally obtained by Ti anodization in a fluoride-containing electrolyte. Here, an oxide layer is formed on Ti surface and then, it is dissolved by the fluoride ions, leading to the generation of cavities.<sup>15</sup>

Lastly, to improve the conducting properties of TiO<sub>2</sub> based materials, metal/non-metal doping has been carried out. Most interestingly, the research of boron-doping has increased during last years. Making a background of some previous works,<sup>14,16</sup> boron has been incorporated into TiO<sub>2</sub> based nanoparticle films for water treatment. By XPS, the non-metal element has been observed to be introduced in substitutional and interstitial positions into semiconductor lattice, producing Ti<sup>3+</sup> donor states. A red-shift in the absorption edge of photoanodes was achieved besides of an increase of photocurrent due to more photogenerated electrons can be transported to current collector. This benefit could be extrapolated to the fabrication of boron-doped TiO<sub>2</sub> nanotubes to produce an increase of photocurrent in the solar device.<sup>17</sup>

Having described the features of photoanode material, the function of a conventional QDSSC can be explained.<sup>2,18</sup> The device is composed by a sensitized photoanode with an adequate amount of chalcogenide, which absorbs the illumination, generating charge carriers. Under an applied potential, electrons are injected to electron conductor via CB and then collected by the back contact. Carriers are flowed to a counter electrode through the external circuit of device. Photogenerated holes accumulated in the sensitizer are transferred to the electrolyte, to renew the injected carriers to TiO<sub>2</sub>, and subsequently, the oxidized electrolyte is regenerated by the cathode (Figure 2). In this way, one cycle of the energy conversion is

completed. Commonly, a polysulfide solution (S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup>) based on sulfide ions and sulfur is used to avoid the photodecomposition of chalcogenides. The QDs exposition generates a photovoltage (also known as open-circuit voltage, V<sub>oc</sub>) and photocurrent. Briefly, V<sub>oc</sub> is defined as the energy difference quasi between Fermi level (E<sub>F</sub>) of composite photoanode and the potential redox of electrolyte, while the photocurrent generated by device (called short-circuit current, J<sub>sc</sub>) depends on the charge carrier separation and transport capabilities of photoanode. The J<sub>sc</sub> can be declined by recombination process in the TiO<sub>2</sub>/sensitizer/electrolyte interface, decreasing the number of carriers to reach the back contact.

**Figure 2.** Operation principle of interfacial charge carrier mobility process into a QDSSC.



On the other hand, during device assembly, TiO<sub>2</sub> nanotubes based photoanodes grown on the Ti substrate can be used.<sup>19</sup> The prepared material is opaque, which promotes the reverse illumination (through the cathode) into the solar cell. Nonetheless, the cathode material (usually Cu<sub>2</sub>S on conducting glass) and the polysulfide solution are considered as light attenuators, decreasing the light intensity that photoanode must receive to perform an efficient energy conversion. In this way,

the fabrication of TiO<sub>2</sub> nanotubes standing films and their deposition on transparent substrates have been used as a strategy to facilitate the forward illumination, avoiding the light intensity loss.<sup>19,20</sup>

Relating to the deposition methods to carry out the preparation of chalcogenides for the QDSSCs, the successive ionic layer adsorption and reaction (SILAR) has been the most used method because of the facile chemical manipulation, low cost, and facile control of the nanoparticle size of QDs to adjust their optical properties. This allows to promote a high coverage of photoanodes for intensifying the light absorption.<sup>21</sup> Here, the photoanodes are dipped into a cationic and anionic solutions separately (using water or alcohol as solvents) and rinsing the materials with the solvent between each immersion.<sup>12,19</sup> The latter avoids the formation of agglomerates which can affect negatively the PCE of devices.

The deposition of binary chalcogenides during simple sensitization or also co-sensitization processes has been shown as the suitable alternative to harness a high portion of the entire solar spectra, which represents a high benefit to the generation of charge carriers to be transported into the device.<sup>6,8–10</sup> However, binary sensitizers limit their onset absorption to a fixed band gap value (when there is not a high nanoparticle size distribution after preparation), and some cases, their relative band edge positions generate a poor band alignment, for instance, with TiO<sub>2</sub> or other chalcogenides.<sup>2,10</sup> The latter causes a quenching into the composite photoanode, increasing the recombination rate and thereby the decrease of conversion efficiency. Some reports have performed the sensitization process with ternary alloy chalcogenides, where the sensitizer is commonly composed by one cation and two ions or vice versa.<sup>22–24</sup> By modulating the stoichiometry of the constituents into the ternary QDs, their band edges can be easily tuned to form an II-type heterojunction, in a cascade type structure for a facile charge carrier separation and mobility. This kind of materials have been used as an interlayer to generate a pathway for photogenerated carriers from an outer sensitizer to TiO<sub>2</sub> and increase the photovoltaic performance of QDSSCs. Nonetheless, it is not common the reports about the preparation of ternary alloys as outer light harvesters.<sup>25,26</sup> Here, with the aid of an inner binary sensitizer as CdS (its CB and VB provide an adequate band alignment with TiO<sub>2</sub>), the composition of the ternary alloy can be adjusted to find a balance between improved low-energy harvesting, high exciton dissociation and efficient carrier transport to the back contact.

**Figure 3.** Electron transport mechanism into a QDSSC using  $CdS_{1-x}Se_x/CdSe$  co-sensitized TiO<sub>2</sub> photoanodes. a, b, c and d are ascribed to the different CB and VB edge energy positions according with the S/Se molar ratio of ternary alloy.



About the thermodynamic stability of CdX (X = S, Se, Te),<sup>27</sup> it has been studied to be depending on operating conditions as electrochemical system (photoelectrochemical or photovoltaic cells), type of redox couple to promote charge carrier transfer into the cells, and pH region. In this sense, the CdX based materials can be unstable with respect to anodic or cathodic decomposition. Considering the latter, a n-type electrode is expected to be stable and show a high photoconversion efficiency when its standard potential of anodic decomposition (E<sup>o</sup>AD) is more positive than the standard potential (E<sup>o</sup><sub>redox</sub>) of a redox couple. Hence, n-type CdS or CdSe based photoanodes can be used in presence of polysulfide (S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup>) aqueous solution into QDSSCs due to the sulfide (S<sup>2-</sup>) oxidation proceeds at a more negative standard potential than the values for the relevant reactions for CdS and CdSe (about 0.7 V vs SCE). Because of this, the anodic decomposition of CdX is hindered:

$$CdS \to Cd^{2+} + S + 2e^{-} \qquad E^{o}_{AD} = +0.08 V \qquad (1)$$
  

$$CdSe \to Cd^{2+} + Se + 2e^{-} \qquad E^{o}_{AD} = -0.12 V \qquad (2)$$
  

$$S^{2-} + 2h^{+} \to S^{2-}_{2} \qquad E^{o}_{redox} = -0.71 V \qquad (3)$$

Under these reactions, S<sup>2-</sup> can be adsorbed on the photoanode surface, shielding the lattice ions from solvent molecules and increasing the likelihood to react with photogenerated holes into the chalcogenides. The decomposition potentials of CdX photoanodes are shifted, which increases the stability of abovementioned materials.

# 2.2. The role of boron in the carrier transport improvement of CdSe sensitized B,N,F-TiO<sub>2</sub> nanotubes solar cells

The improvement of photovoltaic energy conversion in organic and inorganic based solar cells using low-cost light harvesters is considered as a hot topic in the photovoltaic field, due to progressive developing of new nanomaterials capable to be both good light absorbers and charge transporters. These devices could be comparable or even superior to the performance of conventional Si based solar cells in later years.<sup>28</sup> Some of promising harvesters are composed by 1D nanostructured photoanodes as TiO<sub>2</sub> nanotubes (TNTs), due to their vertically oriented morphology, electrons flow throughout the harvester.<sup>12,28</sup> However, the photoactivation of pristine TiO<sub>2</sub> with UV light allows only to use 5 % of the solar spectrum, providing a low PCE.<sup>29</sup> One approach to enhance the light absorption of TiO<sub>2</sub> is its chemical modification with non-metal atoms such as nitrogen,<sup>30</sup> fluorine,<sup>31</sup> and boron<sup>16</sup> which incorporate intraband gap energy levels in the wide gap of semiconductor. These levels require a lower energy to photogenerate charge carriers in the solid compared to the band gap of TiO<sub>2</sub> (3.2 eV). In addition, the incorporated energy levels improve conducting properties of TiO<sub>2</sub>, facilitating electron transport into the material.<sup>17</sup>

Another attractive strategy is the TiO<sub>2</sub> sensitization with narrow-band gap semiconductors-based QDs thanks to their optoelectronic properties and tunability to enhance harvesting in a wide range of the visible spectrum. This can be achieved by controlling the QDs size, which results in the formation of band structures. This is one of the critical factors in the efficiency of interfacial charge carrier transfer.<sup>32,33</sup> TiO<sub>2</sub>/QDs assemblies have been studied as light harvesters or photoanodes into QD-sensitized solar cells (QDSSCs), where photogenerated electrons into QDs are transported through TNTs.<sup>12,28,29,32,33</sup>

Although QDs sensitizers show notable characteristics as high extinction coefficient and generation of multiple electron hole pairs by absorption of one photon compared with the organic sensitizers,<sup>12</sup> these trend to exhibit photodecomposition, one of the most important causes for a low photoconversion efficiency (PCE) in QDSSCs.<sup>29,33</sup> Thus, the synthesis of inorganic sensitizers with high photostability and light absorption capability is still a huge challenge in the fabrication of third-generation photovoltaic devices. Cadmium chalcogenides (CC) based QDs like CdS and CdSe have been widely used in QDSSCs, due to they are photostable and form a II-type energy band alignment with TiO<sub>2</sub>, providing a driving force to carry out the separation of photogenerated charge carriers and thereby, the increase the PCE.12,21,29,32 Recently, CdSe has attracted more attention due to its low-band gap around 1.6 -1.7 eV,<sup>21,34,35</sup> leading to a wider visible light absorption range compared with CdS (~ 2.42 eV).<sup>36</sup> However, some works have mentioned about the issue to obtain a wellcovering TiO<sub>2</sub> surface by CdSe QDs,<sup>21,28,37</sup> and the relative positions of conduction band edges of both the CdSe and TiO<sub>2</sub> are not far enough to perform an adequate band alignment.<sup>22,32</sup> These two disadvantages limit light harvesting and electron transport through solar cell. To solve the first problem, SILAR process has been used. This processing in solution not only let to grow well dispersed CC on TiO<sub>2</sub> photoanode surfaces, but also control the QDs particle size, allowing the band engineering of QD to match with  $TiO_2$  to increase the electron flow and PCE into a solar cell.16,36,38

To ensure an efficient light harvesting and electron transport for energy conversion applications, the two abovementioned approaches have been combined. CdS and CdSe have been grown on non-metal doped TiO<sub>2</sub> based photoanodes, establishing a synergistic effect to improve the photoresponse of composites compared with both the TiO<sub>2</sub> and chalcogenides separately.<sup>39-41</sup> However, it has not been described with supported evidences why the synergism between doping and sensitization occurs into the composites, to improve their photo(electro)chemical and photovoltaic performances. Thus, there is an enough scope to take this further. Here, this chapter discusses the influence of boron as co-dopant on the enhancement of light harvesting and carrier transport abilities of CdSe QDs-sensitized B,N,F-tri-doped TNTs (BNF-Y-CdSe). The role of boron allowed to elucidate (1) the main factor to generate the synergistic behaviour into composites, and (2) its effect on the electron injection and transport into BNF-Y-CdSe/electrolyte interface. A charge carrier transport mechanism is proposed to explain the favourability of both the sunlight harvesting and carrier mobility, to increase the PCE of a QDSSC.

# 2.3. Effect of Cd-Cd energy states formation on carrier transport ability into CdS/CdS<sub>1-x</sub>Se<sub>x</sub> quantum dot solar cells

Solar energy collection has been without a doubt, one of the most important research objectives nowadays to mitigate the use of fossil fuels as energy source, which have caused environmental pollution and energy crisis in worldwide. To achieve an efficient sunlight absorption and energy conversion, diverse generations of photovoltaic devices has been studied, highlighting the third-generation QDSSCs.<sup>42</sup> Here, binary transition metal chalcogenides as CdX (X = S, Se and Te), PbS, CulnS<sub>2</sub> among others, have been used as sensitizers<sup>10,42-44</sup> due to high extinction coefficient, tunable band gap (E<sub>g</sub>) controlled by the particle size of QDs, and multiple-charge carrier generation by absorption of a single low energy photon. Considering these essential characteristics, a theoretical photovoltaic efficiency higher than 40 % has

been estimed for this kind of devices,<sup>42</sup> overcoming the Shockley and Queisser limit of 32 %.

An additional feature for the photovoltaic performance of QDSSCs is the photoanode material used as electron conductor. Binary chalcogenides have been deposited on TNTs, where their vertically oriented structure allows the address of photogenerated charge carriers transport in the sensitizers to reach the back contact.<sup>10,26,45</sup> Although the latter features are recognized, a lower PCE is still obtained by QDSSCs. Many reasons have been considered to explain the poor photovoltaic performance of QDSSCs as the use of a sensitizer with a unique band gap, limiting the harvest of entire solar spectral region, and low carrier transfer in the TiO<sub>2</sub>/sensitizer interface.<sup>43</sup> To surpass the latter disadvantages, some modifications have been applied to the photoanode material as (1) the incorporation of impurities into the TiO<sub>2</sub> lattice by doping,<sup>40,46</sup> which increases electron donor states in the oxide semiconductor, and (2) co-sensitization by deposition of two or more binary chalcogenides on the TiO<sub>2</sub> surface, obtaining a wide spectral response.<sup>12,21,47</sup> However, a high proportion of the adsorbed illumination is collected by the outer sensitizer which often does not shows a suitable band structure with the inner one.<sup>22,48</sup> This band edge unmatching blocks electron transport in the formed heterojunction, providing a low PCEs.

A remarkable alternative to reach a balance between an adequate optical band gap and band structure in the composites is the incorporation of ternary alloy QDs. Some reports have pointed out the deposition of CdS<sub>1-x</sub>Se<sub>x</sub> solid solutions by SILAR method, where their optical properties are controlled by tuning the composition of alloy.<sup>22,23,26</sup> To vary the S/Se molar ratio of the CdS<sub>1-x</sub>Se<sub>x</sub> QDs deposited on TiO<sub>2</sub>, a suitable cascade type structure can be formed with other chalcogenides, e.g. CdSe, which improves electron injection from CdS<sub>1-x</sub>Se<sub>x</sub>/CdSe interface to oxide semiconductor.<sup>22-24</sup> Nevertheless, similar to the binary co-sensitization, the sunlight harvesting is restricted by the band gap of binary sensitizer, limiting the photovoltaic performance of the cell. So, ¿can we use a CdS<sub>1-x</sub>Se<sub>x</sub> alloy as an outer sensitizer to absorb a wide solar energy spectrum and increase the electron flow in a composite photoanode? Scarce works have mentioned the influence of outer ternary chalcogenides assembled with binary sensitizers or other alloys, on the PCE of QDSSCs,<sup>25,26,49,50</sup> indicating the rarity of stepwise band structure generated during co-sensitization of TiO<sub>2</sub>.

In spite to use a ternary alloy to enhance the photovoltaic properties of a QDSSC, low PCEs are still achieved, which allows to deduce that an additional issue has not been considered to explain the detriment of the cell performance. Some works in physical chemistry have reported the presence of Cd defects into sensitizers as CdS, promoting the narrowing of its band gap lower than that of bulk.<sup>51,52</sup> These defects, also called as Cd-Cd bondings, are energy levels into chalcogenide, formed by CdS nanoparticle interconnection during SILAR sensitization. The effect of these states on the charge carrier separation and transport abilities into Cd chalcogenide sensitized photoanodes has not been investigated, presuming to be a "silent" factor in the performance of the cells.

Herein, by correlating the photo(electro)chemical and photovoltaic properties of CdS/CdS<sub>1-x</sub>Se<sub>x</sub> co-sensitized boron, nitrogen and fluorine-tridoped TNTs (BNF-Y-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>), this chapter shows the influence of Cd-Cd energy levels on the optical properties and carrier mobility of composites. S/Se molar ratio in the ternary alloy was also studied to attain a suitable way for the electron injection and enhance the PCE of QDSSCs. A charge carrier transfer mechanism was proposed to observe the function of CdS<sub>1-x</sub>Se<sub>x</sub> as an outer sensitizer, and Cd-Cd energy levels into a photovoltaic process, to decrease charge recombination and increase the electron lifetime into materials. This contribution opens the possibilities to clarify the main causes that limit the improvement of PCE in QDSSCs.

# 2.4. Incorporation of Mn-doped CdS quantum dots as an alternative to enhance band structure mismatch into Bi<sub>2</sub>S<sub>3</sub> based solar cells

The PCE has been the most remarkable feature for obtaining a promising solar cell during the last years. However, the research is eventually focused on the improvement of optical properties of several photoanode materials, and the decrease of charge carrier recombination into the device.<sup>53</sup> Without a doubt, by controlling these characteristics, a high energy conversion can be achieved. The latter is the case of QDSSCs, which have reached the PCE of their equivalent dye-sensitized solar cells around 11 %.<sup>3</sup> As soon as the electron conductor/sensitizer interaction was progressively understood, the PCE was increased over 12 %.<sup>54</sup> Advantages of narrow band gap-semiconductor based QDs as generation of multiple electron-hole pairs, high molar extinction coefficient, and tunable band structure have upgraded the sunlight harvesting capability and carrier transport into solar cells.<sup>54,55</sup>

Despite these improvements, some semiconductors do not show one of the latter two abilities. This is the case of a lead-free sensitizer like Bi<sub>2</sub>S<sub>3</sub>. This low-toxic chalcogenide displays a low band gap (E<sub>g</sub>) around 1.2-1.7 eV, meaning a high visible-light absorption.<sup>56,57</sup> Even so, Bi<sub>2</sub>S<sub>3</sub>-based solar cells using TiO<sub>2</sub> based photoanodes have produced PCEs lower than 1.0 %, caused mainly for a poor band alignment in the TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> interface.<sup>58-61</sup> Therefore, the co-sensitization has been reported to be efficient when a suitable band structure between binary sensitizers, for instance, CdS and CdSe, is promoted, which generates a wide spectral response and a facile pathway for the electrons to reach the back contact.<sup>8,21</sup> However, some reports have also demonstrated that the use of CdS as inner sensitizer provides an energy barrier for charge carrier separation and mobility, achieving low PCEs.<sup>22,48,62</sup>

An alternative to overcome the latter issue is the incorporation of Mn<sup>2+</sup> electronic levels into the binary CdS. These species are located close to CB of chalcogenide,

enhancing the charge carrier separation and electron transfer dynamics.<sup>55,63-65</sup> In addition, the Mn<sup>2+</sup> incorporation red-shifts the associated E<sub>9</sub> of the modified photoanodes, which extends the light harvesting to low energies and produce more carriers to be transported.<sup>64-66</sup> The amount of Mn<sup>2+</sup> into CdS plays an important role in the photovoltaic performance, due to an excess of this cation can act as electron traps besides to provide a band alignment mismatch into the composites. Thus, the PCE of a cell is declined.<sup>63,67</sup> Mn<sup>2+</sup> content can be adjusted by adding Mn precursor through SILAR, using alcoholic solutions during the formation of Mn-doped CdS QDs. Furthermore, an adequate amount of Mn<sup>2+</sup> into inner CdS can increase electron lifetime into the composite material, preventing charge carrier recombination and loss of PCE in QDSSCs.<sup>68</sup>

The photovoltaic performance of Mn-CdS sensitized solar cells has been studied in function of added Mn<sup>2+</sup> by current voltage characteristic curves. Higher PCE values than that CdS-devices have been obtained.<sup>64,66,68</sup> Nonetheless, the literature is limited about the use of Mn-CdS in the improvement of band structure mismatch into QDSSCs. By using photoelectrochemistry, light harvesting and charge carrier transportation abilities of composites can be deeply analyzed to predict their favourability in photovoltaic applications. This can contribute to enhance the PCE of Bi<sub>2</sub>S<sub>3</sub>-sensitized solar cells. Herein, the aim of this chapter is correlate the photo(electro)chemical properties of Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> co-sensitized boron, nitrogen and fluorine-tridoped TiO<sub>2</sub> nanotubes (BNF-X-Mn-Y-CdS-Bi<sub>2</sub>S<sub>3</sub>) composites with the amount of Mn<sup>2+</sup>, to provide an efficient pathway for carrier mobility from Bi<sub>2</sub>S<sub>3</sub> to tridoped TiO<sub>2</sub> nanotubes (BNF-TNTs). In this way, electron lifetime and PCE of Bi<sub>2</sub>S<sub>3</sub> based QDSSCs can be improved.

#### 3. EXPERIMENTAL SECTION

#### 3.1. Preparation of BNF-TNTs transparent photoanodes

Vertically oriented boron-doped TiO<sub>2</sub> nanotubes (BNF-TNTs) were grown by Ti anodization in an electrolyte solution containing 0.45 wt % NH<sub>4</sub>F, 2.0 wt % deionized (DI) water in ethylene glycol, using different amount of H<sub>3</sub>BO<sub>3</sub> of 0.04 wt%, 0.06 wt% and 0.09 wt% as boron precursor. A bias potential of 60 V was applied for 2.5 h, in a two-electrode cell. A Cu foil was used as cathode.<sup>46</sup> Prior to anodization process, Ti foils (99.5 % of purity, 5 cm<sup>2</sup>) were polished with various SiC emery papers, separately sonicated in ethanol, acetone and rinsed with DI water, each one for 5 min. Anodized samples were also rinsed with DI water, dried and annealed at 100 °C and 400 °C, respectively, using a heating rate of 3 °C min<sup>-1</sup>. For comparative purposes, N,F-codoped TNTs (NF-TNTs) were grown carrying out the anodization process in absence of H<sub>3</sub>BO<sub>3</sub>.

To obtain NF-TNTs and BNF-TNTs transparent photoanodes, annealed samples underwent second anodization for 15 min, using similar experimental conditions described above. NF-TNTs and BNF-TNTs in form of free standing films were detached from Ti after immersion into 30 wt % H<sub>2</sub>O<sub>2</sub> solution for 10 min. Then, films were adhered to indium-tin oxide (ITO) conductive glass by using a B-TiO<sub>2</sub> sol and dried at room temperature. The procedure of sol preparation is described elsewhere.<sup>16</sup> Lastly, the abovementioned thermal treatment was repeated.

#### 3.2. Deposition of CdSe QDs on BNF-TNTs photoanodes

BNF-TNTs and NF-TNTs photoanodes were sensitized with different CdSe load using SILAR method, conducted into a  $N_2$  filled glove box. The materials were immersed into a 0.03 M CdSO<sub>4</sub>·8/3H<sub>2</sub>O ethanol: water solution (volume ratio 1:1) for 1 min and rinsed with ethanol for 20 s. Then, the photoanodes were dipped into a

0.03 M Se<sup>2-</sup> ethanol solution for 1 min and rinsed again with ethanol for 20 s. The sensitized materials were dried under N<sub>2</sub> atmosphere for several minutes. The drying process was performed cycle by cycle. The Se<sup>2-</sup> solution was prepared by mixing SeO<sub>2</sub> with NaBH<sub>4</sub> in ethanol into the glove box. Details of procedure are mentioned elsewhere.<sup>69</sup>

One SILAR cycle was performed to carry out the two-step dipping in the cationic and anionic solutions. Photoanodes were denominated as X-BNF-Y-CdSe, where X was the amount of H<sub>3</sub>BO<sub>3</sub> (in wt %) used during BNF-TNTs films growth and Y, the number of SILAR cycles of CdSe deposited on nanotubes (Y = 3, 4, 5 and 6). To estimate the PCE of the composite photoanodes in a sensitized solar cell, a ZnS passivation layer was deposited on CdSe-sensitized nanotubes without B-doping (NF-Y-CdSe) and BNF-Y-CdSe by SILAR after 2 cycles. Aqueous solutions of 0.1 M Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O and 0.1 M Na<sub>2</sub>S were used as Zn<sup>2+</sup> and S<sup>2-</sup> sources, respectively. Samples were rinsed with DI water during the rinsing steps of SILAR. Lastly, the materials were dried at air and annealed at 250 °C for 1 h using a heating rate of 3 °C min<sup>-1</sup>

#### 3.3. CdS QDs-sensitization of BNF-TNTs photoanodes

CdS QDs-sensitized BNF-TNTs photoanodes were obtained by SILAR, dipping the BNF-TNTs into a cationic solution containing 0.5 M CdSO<sub>4</sub>·8/3H<sub>2</sub>O methanol: water solution (volume ratio 1:1) for 1 min, followed by rinsing with methanol for 30 s. Then, the materials were immersed into a 0.5 M Na<sub>2</sub>S methanol: water anionic solution (volume ratio 1:1) for 1 min. Sensitized BNF-TNTs were again rinsed with methanol for 30 s. The latter two-step dipping into the Cd<sup>2+</sup> and S<sup>2-</sup> methanol precursors was considered as one SILAR cycle. Diverse number of SILAR cycles (Y = 2, 3, 4, and 5 cycles) were conducted during sensitization to deposit different load of CdS on BNF-TNTs, denominated as BNF-Y-CdS. Composites were annealed at 250°C for 2 h at 3°C min<sup>-1</sup>.

#### 3.4. CdS<sub>1-x</sub>Se<sub>x</sub> QDs-sensitization of BNF-Y-CdS photoanodes

CdS<sub>1-x</sub>Se<sub>x</sub> alloy QDs were grown on BNF-4-CdS by using a N<sub>2</sub>-filled glove box as it is described elsewhere<sup>22</sup> with a slight modification. Briefly, 4-CdS materials were immersed into 0.03 M CdSO<sub>4</sub>·8/3H<sub>2</sub>O ethanol: water cationic solution (volume ratio 1:1) and then separately dipped into the several molar concentrations of both Na<sub>2</sub>S ethanol: water solution (volume ratio 1:1) and Se<sup>2-</sup> ethanol solutions, each one for 30 min. After the immersion into each SILAR precursor, materials were rinsed with ethanol for 30 s. The sum of concentrations between both the S<sup>2-</sup> and Se<sup>2-</sup> anionic solutions was equal to the concentration of Cd<sup>2+</sup> source (0.03 M). In this way, the S/Se molar ratio was varied from 2.0, 1.0, 0.5 to 0, by increasing the Se content in the ternary alloy. Nominal compositions of CdS<sub>0.67</sub>Se<sub>0.33</sub>, CdS<sub>0.50</sub>Se<sub>0.50</sub>, CdS<sub>0.33</sub>Se<sub>0.67</sub> and CdSe, were obtained, respectively. Five SILAR cycles were used during CdS<sub>1-x</sub>Se<sub>x</sub> sensitization. Materials were denominated as BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>. A ZnS layer was deposited on the composites denominated as BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> by two-SILAR cycles, from Zn<sup>2+</sup> and S<sup>2-</sup> aqueous cationic and anionic solutions composed by 0.1 M Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O and 0.1 M Na<sub>2</sub>S. Prepared materials were annealed at 250°C for 2 h.

#### 3.5. Mn-doped CdS/Bi<sub>2</sub>S<sub>3</sub> QDs co-sensitization of BNF-TNTs

The deposition of Mn-CdS QDs on BNF-TNTs was carried out by SILAR method, where BNF-TNTs/Ti photoanodes were separately dipped into diverse concentrations of cationic solutions composed by CdSO<sub>4</sub>·8/3H<sub>2</sub>O in methanol: water solution (volume ratio 1:1) and MnCl<sub>2</sub> in methanol, each for 30 s, followed by rinsing with methanol for 30 s after each deposition. Then, Cd<sup>2+</sup>/Mn<sup>2+</sup>-materials were immersed into an anionic solution consisting of 0.5 M Na<sub>2</sub>S in methanol: water solution (volume ratio 1:1) for 1 min. Nominal Cd/Mn molar ratio was varied to be 1.5, 1.0 and 0.7 by increasing the Mn content into the Mn-CdS based sensitizer. The sum of concentrations of both Cd<sup>2+</sup> and Mn<sup>2+</sup> cationic solutions was equal to the

concentration of S<sup>2-</sup> source (0.5 M). Diverse number of SILAR cycles (3, 4 and 5 cycles) were performed during Mn-CdS sensitization, where the latter three-step immersions of BNF-TNTs into each Cd<sup>2+</sup>, Mn<sup>2+</sup> and S<sup>2-</sup> precursors was one SILAR cycle. During the determination of the suitable load of deposited Mn-CdS QDs in the sensitization process, composites were denominated as BNF-Mn-Y-CdS (or simply Mn-Y-CdS), where Y was the number of SILAR cycles. Here, the Cd/Mn molar ratio into Mn-CdS was fixed to 1.5. Then, the amount of Mn<sup>2+</sup> was varied, labelling the composites as BNF-X-Mn-CdS (or simply X-Mn-CdS), where X was the atomic percentage of Mn<sup>2+</sup> into CdS (determined by XPS, see below).

For BNF-TNTs/ITO, Mn-CdS was deposited using the Cd/Mn molar ratio of 1.0 and then the anionic solution. Undoped CdS was also deposited on BNF-TNTs for comparative purposes, achieving the latter procedure in absence of MnCl<sub>2</sub>. Bi<sub>2</sub>S<sub>3</sub> QDs was deposited on BNF-Mn-CdS/Ti and BNF-Mn-CdS/ITO, dipping separately each material into 0.4 M Bi(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> in ethanol as cationic precursor, and 0.4 M Na<sub>2</sub>S in an water: ethanol solution (volume ratio 1:1) as anion source for 1 min. Photoanodes on ITO were passivated with ZnS layer by SILAR, immersing the materials into aqueous solutions of 0.1 M Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O and 0.1 M Na<sub>2</sub>S as cationic and anionic precursor, respectively. Two SILAR cycles were achieved to form Bi<sub>2</sub>S<sub>3</sub> and ZnS. As-prepared samples were annealed at 250 °C for 1 h. After Bi<sub>2</sub>S<sub>3</sub>, the composite materials were denominated as BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub>.

#### 3.6. Physicochemical characterization of photoanodes

The surface of sensitized photoanodes was observed by FESEM, FEI Quanta 650 FEG. The characteristics planes and particle size of deposited chalcogenides on BNF-TNTs were determined by TEM and HR-TEM, with a Tecnai F20 Super Twin TMP. During acquisition of images, a 200 kV-acelerating voltage was used. Reflectance spectra of materials were obtained with a Shimadzu PC 2401 UV-Vis spectrometer, in a wavelength range between 200 to 800 nm. A confocal

high-resolution Raman microscope with a 532 nm green laser was used to achieve the characteristic vibrations of the sensitizers. The corresponding Raman spectra of BNF-TNTs before and after CdSe, CdS/CdS<sub>1-x</sub> Se<sub>x</sub>, Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> sensitizations were obtained with spot of 1 µm in the wavenumber range of 100-1000 cm<sup>-1</sup>. An integration time 5 s and 100 scans were swept during measurements. Survey and HR-XPS spectra of the elements contained in the composites were achieved with a SPECS Phoibos 150 spectrometer equipped with a hemispheric analyser. Typical binding energies (BEs) of the elements and decomposed peaks in the XPS spectra were fixed with the C 1s signal at 284.6 eV, using an Al anode with an X-ray energy of 1486.6 eV. Shirley background based on a mixed Gaussian-Lorentzian function (70:30) was applied to decompose the HR-XPS N 1s, F 1s, B 1s, Ti 2p, Cd 3d, S 2p, Se 3p, Se 3d, Mn 2p and Bi 4f.

#### 3.7. Photo(electro)chemical measurements of photoanodes

**3.7.1. CdSe QDs-sensitized BNF-TNTs photoanodes.** Photoelectrochemical properties of BNF-TNTs grown on Ti (X-BNF-TNTs/Ti) and BNF-Y-CdSe composites adhered on ITO glass were studied in a three-electrode cell, using an Autolab PGSTAT 302N potentiostat. An Ag/AgCl, 3 M KCl electrode (+ 210 mV vs NHE) and a graphite rod (AGKSP grade) were used as reference electrode and counter electrode, respectively. The electrolyte solution was 1.0 M Na<sub>2</sub>S (pH 12) deaerated with N<sub>2</sub> bubbling for 20 min. The illumination source was a halide lamp with a light intensity of 60 mW cm<sup>-2</sup>. The emission spectrum of the light source is shown in Appx. A. Photopotential measurements were conducted at open circuit varying the number of light on/off cycles. Photovoltammetry measurements were obtained under a bias potential (OCP) at 10 mV s<sup>-1</sup>. Photocurrent transients were obtained under a bias potential of 0.45 V during five on/off light cycles. Electrochemical impedance spectroscopy (EIS) measurements were carried out under dark and illumination conditions at OCP, in a frequency range of 10 kHz to 0.01 Hz using modulation amplitude of 10 mV. Mott Schottky (M-S) analyses were conducted from -1.2 V to

0.3 V in negative direction, at a frequency value of 616 Hz. Semiconducting properties as charge carrier density (N<sub>d</sub>) and the flatband ( $E_{fb}$ ) were determined to vary the amount of H<sub>3</sub>BO<sub>3</sub> into the BNF-TNTs.

**3.7.2.** CdS and CdS/CdS<sub>1-x</sub>Se<sub>x</sub> QDs-sensitized BNF-TNTs photoanodes. The effect of CdS load and the variation of S/Se molar ratio in the ternary alloy, on the photo(electro)chemical properties of BNF-Y-CdS and BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>, were investigated in a three-electrode cell using an electrolyte solution containing N<sub>2</sub>-bubbled 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12). An Autolab 302N potentiostat was employed to carry out the photopotential and electrochemical characterization. A graphite rod (AGKSP grade) and an Ag/AgCl, 3 M KCl were used as counter electrode and reference electrode, respectively. OCP curves of the composites were achieved by illuminating the samples during 600 s during two-light on/off cycles. EIS spectra were obtained under illumination at OCP, in frequency ranges from 10 kHz to 0.01 Hz for the BNF-Y-CdS, and 20 kHz to 0.01 Hz for BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>, using an amplitude of 10 mV. The light source was a halide lamp of 60 mWcm<sup>-2</sup>.

**3.7.3. Mn-CdS and Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> QDs-sensitized BNF-TNTs photoanodes.** The influence of Mn-CdS load and amount of Mn<sup>2+</sup> on the photo(electro)chemical and semiconducting properties of BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites was studied in a three-electrode cell coupled with an Autolab PGSTAT 302N. A N<sub>2</sub>-bubbled 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> redox couple was used as electrolyte solution (pH 12). Composites, an AGKSP-type graphite rod and Ag/AgCl, 3 M KCl were employed as working, counter and reference electrodes, respectively. The visible-light source was a 150 W halide lamp with UV-block (60 mWcm<sup>-2</sup>). OCP curves were performed interrupting the illumination of composites twice during 600 s. Photovoltammetry curves were conducted at 10 mV s<sup>-1</sup> from open circuit. Photocurrent transients were attained after 660 s, during five light on/off cycles, applying a bias potential of 0 V<sub>Ag/AgCl</sub>. EIS spectra were obtained under visible light at open circuit, in a frequency range of 100 kHz to 0.01 Hz, with an amplitude signal of 10 mV. M-S plots were
achieved under dark conditions, in negative direction from -1.0 to 0.7  $V_{Ag/AgCI}$  at 517 Hz.

## 3.8. Assembly of solar cells

QDs-sensitized solar cells using BNF-Y-CdSe. BNF-Y-CdS. the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>. BNF-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> and BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites were fabricated assembling the photoanodes with Cu<sub>2</sub>S/Cu based cathodes, which were prepared modifying a procedure reported elsewhere.<sup>70</sup> In the case of BNF-Y-CdS based solar cells, CuS/FTO cathodes were also used for comparative purposes. Briefly for Cu<sub>2</sub>S/Cu, Cu foils were polished with diverse silicon carbide papers, rinsed with acetone and DI water, each for 5 min and dried under ambient conditions. Metal samples were immersed into an aqueous polysulfide solution composed by 1.0 M Na<sub>2</sub>S + 1.0 M S for 20 min. A black film was formed on the Cu surface, indicating the formation of Cu<sub>2</sub>S coating.<sup>70</sup> In the case of CuS/FTO, cathodes were obtained by the spray pyrolysis method, where a spray solution composed by Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O and CS(NH<sub>2</sub>)<sub>2</sub> in a Cu:S molar ratio of 1:2 was deposited on pre-treated FTO substrates at a spray deposition rate of 7 mL min<sup>-1,71</sup> Current-voltage (J-V) performance curves were obtained by using a Keithley 4200 source meter at 50 mV s<sup>-1</sup> for BNF-Y-CdS and 100 mV s<sup>-1</sup> for the other composites photoanodes. The exposed area of composites was 0.23 cm<sup>2</sup>, which was illuminated with an Oriel sol 3A sun simulator calibrated with a 91150V Si reference cell to establish 1 sun conditions (AM 1.5 G, 100 mWcm<sup>-2</sup>). A black plastic tape mask was attached on top of materials to avoid the light scattering. Photovoltaic parameters as short-circuit current ( $J_{sc}$ ), open-circuit potential ( $V_{oc}$ ), fill factor (FF) and photoconversion efficiency (PCE) were determined from J-V curves.

## 4. RESULTS AND DISCUSSION

## 4.1. CdSe QDs-sensitized BNF-TNTs photoanodes

4.1.1 Morphological and physicochemical characterization of X-BNF-Y-CdSe **photoanodes.** The formation of a  $TiO_2$  nanotubular structure is essential to facilitate charge carrier separation and transport in the photovoltaic process.<sup>12,13,17</sup> Nevertheless, the light harvesting in a photovoltaic device depends on light intensity that the photoanode receives to produce charge carriers. In this sense, the fabrication of semitransparent photoanodes based on free-standing films can favour forward illumination into a solar cell, decreasing the loss of light intensity observed by reverse illumination.<sup>12,19</sup> To ensure the existence of nanotubes in the freestanding films, typical FESEM images of 0.06-BNF-TNTs are shown in Fig. 4, where top-view (Fig. 4a) and the cross-section (Fig. 4b) of materials were observed. A highly-ordered structure was produced after Ti anodization and this arrangement was remained after BNF-TNTs films detachment. The average pore diameter was estimated to be around  $118.0 \pm 4.1$  nm, while the wall thickness of BNF-TNTs was around  $18.2 \pm 4.3$  nm. From the cross-section view, BNF-TNTs arrays are compact and vertically aligned, with an average tube length of  $16.8 \pm 1.0 \mu m$ . The detached BNF-TNTs in form of a free-standing film (inset of Fig. 4a) shows a light-yellow coloration and it is translucence.

**Figure 4.** Top view and cross section FESEM images for 0.06-BNF-TNTs photoanode a,b) before and c,d) after 5-CdSe sensitization.



After depositing the BNF-TNTs films on the ITO substrate, the CdSe QDs sensitization of photoanodes by SILAR was carried out. Fig. 4c exhibits the typical top-view image of 0.06-BNF-5-CdSe photoanode. It can be observed a decrease of TNTs pore diameter and the sealing of tube interspace. For this case, the average pore diameter and wall thickness were  $109.5 \pm 5.3$  nm and  $48.2 \pm 6.4$  nm, respectively. After growing TNTs with long cavities and small wall thickness, the SILAR ethanol cationic and anionic precursors can penetrate easily into the inner side of TNTs and among the tube interspace.<sup>69</sup> Therefore, BNF-TNTs depicts a well-covered and rougher surface than that of pristine NF-TNTs (See Fig. 4d). It has been claimed that a non-uniform surface with low CdSe QDs load is achieved to use the SILAR method.<sup>37</sup> Here, it was demonstrated to use the corresponding SILAR

precursors, the BNF-TNTs pores and the outer side of tubes can be well-covered with the spherical-type CdSe nanoparticles.

The 0.06-BNF-5-CdSe photoanode was also investigated by TEM. Fig. 5a displays a low-magnification TEM image, where a nanotubular structure with dispersed small nanoparticles along the TNTs was achieved. To extend the magnification (Fig. 5b), it was seen the interspace of TNTs was filled with nanoparticles among the tube, which generated a well-covered surface. Fig. 5c depicts the typical HR-TEM image of the composite material, where the preferential planes or orientations of TiO<sub>2</sub> and the sensitizer were estimated. By comparing carefully the lattice parameters with the PDF-2 (000-71-66) card of the International Centre for Diffraction Data (ICDD), the interplanar spacing around 0.35 nm was attributed to the (101) plane from the anatase phase in 0.06-BNF-TNTs,<sup>12,17</sup> while the lattice fringe of 0.29 nm was ascribed to the (200) plane from CdSe QDs.<sup>47</sup> The distribution of nanoparticle size on the BNF-TNTs was determined to be around 5.80  $\pm$  0.05 nm. The size of five nanoparticles was measured to obtain the corresponding average value. This is an indication of CdSe nanoparticles are in the scale of QDs.

**Figure 5.** a) Typical TEM image of 0.06-BNF-5-CdSe photoanode. b) Large magnification and c) HR-TEM image of composite material. d) Raman spectra of 0.06-BNF-TNTs before and after 5-CdSe sensitization. A and C labels indicate Raman peaks of anatase and CdSe, respectively.



The composition and presence of crystalline phases in materials are commonly achieved by conventional X-ray diffraction. However, the use of this technique on this kind composites does not generate information due to a pattern is not detectable by the small nanoparticles covering the nanotubes.<sup>72</sup> Hence, Raman spectroscopy was performed on the 0.06-BNF-5-CdSe photoanode (Fig. 5d). The Raman spectrum of 0.06-BNF-TNTs photoanode before sensitization displayed five peaks at 145.5 cm<sup>-1</sup>, 196.8 cm<sup>-1</sup>, 394.7 cm<sup>-1</sup>, 516.3 cm<sup>-1</sup> and 634.8 cm<sup>-1</sup>, associated to the anatase phase. After CdSe sensitization, the main peak at 145.5 cm<sup>-1</sup> decreased in

intensity and four new peaks appeared at (207, 270.2, 412.3 and 471.5) cm<sup>-1</sup>. The first peak was attributed to longitudinal (LO) phonon, while the second and fourth ones were ascribed to 2LO and 3LO overtones, respectively. Lastly, the third peak was associated to overlapped bands corresponding to LO + surface optical phonon.<sup>72,73</sup> The results confirmed the CdSe QDs deposition on the BNF-TNTs surface by SILAR.

To observe changes in the optical properties of BNF-TNTs and BNF-Y-CdSe photoanodes (Fig. 6), their corresponding band gap (Eg) values were estimated through the modified Kubelka-Munk (K-M) approach from reflectance spectra (Table 1). Fig. 6a displays the Eg of 0.06-BNF-TNTs before and after Y-CdSe sensitization. All X-BNF-TNTs photoanodes exhibited two slopes in the K-M curves associated to two different  $E_g$  (named  $E_{g1}$  and  $E_{g2}$ ). These values are lower than intrinsic E<sub>g</sub> for TiO<sub>2</sub> (3.2 eV), which means the co-existence of intra band gap energy levels.<sup>16,30,31</sup> By comparing the K-M curves, it was observed that band gaps of NF-TNTs was not appreciably shifted after boron doping, although the K-M F(R) function was increased. It is well known that N and F can be incorporated into TNTs during their growth, producing an N,F-co-doping. Nitrogen can generate N 2p intra band gap levels, while fluoride ions can generate Ti<sup>3+</sup> donor species.<sup>30,31</sup> Thus, it can be suggested that, the photoactivation energies around 2.86 eV and 2.34 eV for the bare NF-TNTs corresponded to electron excitation from N 2p levels to the conduction CB of semiconductor, and the Ti<sup>3+</sup> states, respectively.<sup>30,74</sup> This modification allowed the photoactivation of TNTs under visible light. In addition, it has been claimed that the presence of boron into TiO<sub>2</sub> also generates Ti<sup>3+</sup> states, which causes the enhancement of visible-light absorption in B-doped TiO<sub>2</sub> photoanodes.<sup>16,70</sup> The increment of F(R) function indicated that a higher amount of Ti<sup>3+</sup> species was formed into X-BNF-TNTs than that bare NF-TNTs.<sup>14</sup>

After Y-CdSe SILAR sensitization, the composite photoanodes depicted a change in the  $E_g$  (Fig. 6b), indicating an improvement in the visible-light harvesting (Table 1).

The low  $E_g$  of BNF-Y-CdSe materials is characteristic of high extinction coefficient of CdSe, which requires low-energy photons to photogenerate charge carriers. The  $E_g$  of bulk CdSe has been reported to be around 1.6-1.7 eV,<sup>21,33,35</sup> which validates the existence of QD-type small CdSe nanoparticles. The  $E_g$  modification was accompanied with a change in the colour of composite photoanode to increase the SILAR cycles (Fig. 6c). It has been reported that to increase the number of SILAR immersions, the particle size of sensitizer is increased as product of QDs agglomeration. This leads to the formation of continuous band energies from discrete ones into the sensitizer, narrowing its band gap. This effect is known as quantum confinement,<sup>75,76</sup> which allows the modification of the optical properties in CC QDs deposited on TiO<sub>2</sub>. The inherent band gap change during SILAR sensitization causes the band edge rearrangement in the TiO<sub>2</sub>/sensitizer interface, which can enhance or restrain charge carrier transport into the composite.<sup>75</sup> According with the latter, the particle size of CdSe QDs by varying the SILAR cycles could be determined by the Brus equation (4):<sup>77</sup>

$$E_{g,QD} = E_{g,bulk} + \frac{h^2}{8r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$
(4)

where  $E_{g,QD}$  is the optical bang gap of CdSe QDs,  $E_{g,bulk}$  is the band gap associated with the CdSe bulk (1.6 eV),<sup>35</sup> h is the Plank constant, r is the radius of CdSe QDs, and m<sub>e</sub>\* and m<sub>h</sub>\* are the effective mass of electrons and holes in CdSe, respectively. By using the eq. 1, the diameters of CdSe QDs were 4.43 nm, 5.0 nm, 5.58 nm and 7.90 nm for 3-CdSe, 4-CdSe, 5-CdSe and 6-CdSe QDs, respectively. To compare the diameter values of 5-CdSe QDs estimated by eq. 1 and HR-TEM analysis, there is a good accordance, which allowed to confirm the intimate relationship between the E<sub>g</sub> and particle size of CdSe QDs. **Figure 6.** Kubelka-Munk approach for  $E_g$  estimation in a) X-BNF-TNTs and b) 0.06-BNF-Y-CdSe photoanodes. c) Photographs of the Y-CdSe sensitized 0.06-BNF-TNTs varying the number of SILAR cycles.



**Table 1.** Eg values obtained from K-M curves for X-BNF-TNTs and0.06-BNF-Y-CdSe photoanodes.

Before sensitization		After sensitization		
Amount of H <sub>3</sub> BO <sub>3</sub>	E <sub>g1</sub> / eV	E <sub>g2</sub> / eV	SILAR cycles	Eg / eV
0	2.86	2.34	3	1.79
0.04 wt%	2.82	2.39	4	1.75
0.06 wt%	2.83	2.36	5	1.72
0.09 wt%	2.87	2.38	6	1.66

After probing the presence of CdSe QDs on the BNF-TNTs, Fig. 7 shows the XPS analysis performed to 0.06-BNF-5-CdSe, in order to observe the chemical composition and state of each element contained into the material. Elemental survey (Fig. 7a) corroborated the presence of C, O, Ti, Cd and Se. B, N and F were not seen in the general spectra. This indicates the low amount of these elements added after the anodization process. Thus, elemental survey and high resolution XPS spectra of B 1s, N 1s, F 1s and Ti 2p were obtained for 0.06-BNF-TNTs photoanode to observe the influence of the latter elements on the chemical environment of Ti species before the CdSe sensitization.

Fig. 7b depicts the typical high-resolution (HR) XPS C 1s spectrum commonly obtained for TNTs based photoanodes. Three contributions were decomposed at (284.6, 286 and 288.4) eV, associated to the carbon contamination.<sup>16,78</sup> The HR-XPS N 1s spectrum of 0.06-BNF-TNTs is shown in Fig. 7c, where two contributions were observed at 399.3 eV and 401.1 eV. The first signal was associated to the substitutional N into TiO<sub>2</sub>, forming N-Ti-O type bonds, while the second signal was attributed to the interstitial N generating a N-O-Ti type structure into the semiconductor lattice.<sup>30,31,79,80</sup> Moreover, an unique F 1s peak was seen at 684.2 eV, corresponding to the incorporation of substitutional fluoride into TiO<sub>2</sub> (Fig. 7d). According with the similar ionic radius between O<sup>2-</sup> and F<sup>-</sup>, the oxygen positions can be easily swapped by fluoride ions. The latter N and F contributions have been assigned during the XPS studies for N,F-co-doped TiO<sub>2</sub> photoanodes.<sup>30</sup> B 1s peak observed at 191.2 eV (Fig. 7e) corresponded to boron introduced into interstitial positions of TiO<sub>2</sub> lattice, which is characteristic from B-TiO<sub>2</sub> based materials.<sup>14,16,70,81</sup>

The effect of B, N and F on the chemical states of Ti species into 0.06-BNF-TNTs was seen in the curve-fitted HR XPS Ti 2p spectrum (Fig. 7f). Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  doublets were well fitted to add three different type of species during the spectrum decomposition. The BE of each component estimated in this analysis agrees with those values reported elsewhere.<sup>16,82</sup> Doublets at 458.2/464 eV were related to Ti<sup>4+</sup>

species from the TiO<sub>2</sub> lattice, while the peaks at 457/462.1 eV were ascribed to the presence of Ti<sup>3+</sup>. Peaks at 459.7/464.8 eV were associated to the Ti-F bond,<sup>83</sup> validating the chemical specie observed in F 1s spectrum. Both the interstitial B and substitutional F can donate valence electrons to Ti<sup>4+</sup> which induces the formation of Ti<sup>3+</sup> donors.<sup>16,30,31</sup> However, the current analysis did not provide information about the fraction of Ti<sup>3+</sup> separately produced by B and F-modification. Thus, the fraction of Ti<sup>3+</sup> was also estimated for a bare NF-TNTs from the XPS Ti 2p spectrum, achieving 1.23 % of Ti<sup>3+</sup> species.<sup>80</sup> In this study, the amount of Ti<sup>3+</sup> was around 1.72 % for the 0.06-BNF-TNTs, which means an increment of donor species after B-doping. This corroborates the rise of K-M F(R) function of 0.06-BNF-TNTs as an indirect measure of visible-light absorption improvement. Despite the N-modification did not promote the generation of Ti<sup>3+</sup>, the presence of N intra band gap levels into TiO<sub>2</sub> produces a decrease in E<sub>9</sub>. Hence, the chemical modification of TiO<sub>2</sub>.

After 5-CdSe sensitization, the HR-XPS Cd 3d (Fig. 7g) and Se 3d (Fig. 7h) spectra were achieved. For Cd 3d spectrum, the typical Cd  $3d_{5/2}$  and Cd  $3d_{3/2}$  doublets were observed at 404.8 eV and 411.6 eV, respectively. The Se 3d spectrum was fitted with the inclusion of two components at 53.4 eV and 54.2 eV, associated to the characteristic Se  $3d_{5/2}$  and Se  $3d_{3/2}$  doublets. The presence of CdO or/and SeO<sub>2</sub> were not detected, which means the successful formation of CdSe on 0.06-BNF-TNTs.<sup>84,85</sup>

**Figure 7.** a) XPS survey of 0.06-BNF-5-CdSe composite, HR-XPS b) C 1s, c) N 1s, d) F 1s, e) B 1s and f) Ti 2p of 0.06-BNF TNTs before 5-CdSe sensitization. HR XPS g) Cd 3d and h) Se 3d of photoanode after 5-CdSe sensitization.



**4.1.2.** Photo(electro)chemical properties of X-BNF-Y-CdSe composites. The effect of amount of H<sub>3</sub>BO<sub>3</sub> on the photochemical (PC) and photoelectrochemical (PEC) properties of BNF-TNTs is shown in Fig. 8. The open circuit response (E<sub>oc</sub>) of photoanodes depicted a displacement of potential towards more negative values upon illumination (Fig. 8a). This shift indicates the accumulation of electrons in n-type semiconductor solid,<sup>16</sup> which is conserved after boron doping. By irradiating

the BNF-TNTs photoanode grown with 0.04 wt% H<sub>3</sub>BO<sub>3</sub> (blue line), a more negative potential was observed than that bare NF-TNTs (black line). However, to exceed the amount of H<sub>3</sub>BO<sub>3</sub> to 0.06 wt% (red line) and 0.09 wt% (green line), a less negative potential was achieved. According with typical HR-XPS B 1s and Ti 2p spectra of X-BNF-TNTs explained above, the presence of interstitial boron into NF-TNTs increases the fraction of Ti<sup>3+</sup> located below the conduction band of semiconductor. By using a 0.04 wt% H<sub>3</sub>BO<sub>3</sub>, an adequate interstitial boron content can be introduced, generating enough Ti<sup>3+</sup> states to increase the number of electrons in the photoanode. This explains the depletion layer (W) compaction after boron modification (Appx. B),<sup>86,87</sup> improving the conducting properties of NF-TNTs.

Contrarily, a higher amount of interstitial boron could also produce an excess of Ti<sup>3+</sup> states acting as recombination sites.<sup>16</sup> The latter causes a poor charge carrier separation which decreases the photochemical (PC) performance of the materials. The presence of these species was observed during the slow open circuit potential decay after light was turned off, indicating the increase of charge carrier recombination rate into the BNF-TNTs.<sup>12</sup> In spite of the detriment of PC response by a high amount of Ti<sup>3+</sup>, the spatial charge carrier separation into the X-BNF-TNTs photoanodes was improved by applying an external potential, enhancing their photoresponse under illumination. The PEC performance of the B-modified photoanodes was evaluated by photovoltammetry and chopped-light chronoamperometry. The photocurrent generation to apply a potential sweep is shown in typical photovoltammograms for the X-BNF-TNTs photoanodes by varying the amount of H<sub>3</sub>BO<sub>3</sub> (Fig. 8b). The dark current for the materials was negligible (red dash line). Photovoltammograms for NF-TNTs was achieved for comparative purposes. Upon illumination, an increase of photocurrent was obtained in all samples, indicating the charge carrier separation and electron transport from the photoanode/electrolyte interface to the current collector.<sup>30,80</sup>

However, the ability of photoanodes to produce photocurrent was affected to vary the amount of  $H_3BO_3$ . By increasing the amount of  $H_3BO_3$  until 0.06 wt%, the highest photocurrent was reached. Nonetheless, exceeding this amount, the photoresponse of the photoanodes was decreased about twice with respect to the highest photocurrent. This tendency was pointed out in terms of a suitable amount of Ti<sup>3+</sup> produced by the presence of interstitial boron, which was achieved to use 0.06 wt% H<sub>3</sub>BO<sub>3</sub>. Unlike photopotential measurements, a higher H<sub>3</sub>BO<sub>3</sub> content than that of 0.04 wt% can promote an increase of charge carriers separated and transported through the photoanode, improving its light harvesting and PEC performance.<sup>17</sup> Conversely, to surpass the adequate amount of H<sub>3</sub>BO<sub>3</sub>, a clear decrease of the photocurrent is caused by the excessive Ti<sup>3+</sup>. Here, electron-hole pair recombination is favoured, which diminishes the possibility for electrons to reach the current collector. The influence of H<sub>3</sub>BO<sub>3</sub> content on the light harvesting and charge carrier transport abilities into X-BNF-TNTs photoanodes was also observed in chronoamperometric curves obtained under chopped light at 0.45 V<sub>Aq/AqCl</sub> (Fig. 8c). An increase of photocurrent was rapidly achieved due to the electron-hole pair generation and separation, where the electrons were diffused to the current collector.<sup>16</sup> However, a current spike followed by a low current decay were observed during the photocurrent transients upon illumination, indication of the unavoidable electron-hole recombination.<sup>80,86</sup>

When charge carrier generation and recombination rate attained equilibrium, a steady-state photocurrent was reached. Once the light was turned off, the current dropped almost to zero, without decay tails. This was attributed to efficient address of electron transport into photoanodes due to the well-oriented structure of TNTs.<sup>17,80</sup> In addition, the photocurrent produced in each transient kept almost constant, associated to the high stability of materials. After five on-off cycles, X-BNF-TNTs displayed the same trend during the photovoltammetry measurements, where a higher photocurrent was achieved with the 0.06-BNF-TNTs photoanode in comparison with the other boron-doped photoanodes. The result confirmed the

improvement of visible-light absorption, efficient electron-hole pair separation and electron mobility through TNTs after boron modification. The excess of Ti<sup>3+</sup> species formed after boron doping decreased the photocurrent, which means that the charge carrier recombination assisted by these donor states dominates on the PEC performance of 0.09-BNF-TNTs photoanode.

The detriment or improvement of the PEC performance of X-BNF-TNTs by the increase of Ti<sup>3+</sup> after boron doping, indicate a change in the semiconducting properties of NF-TNTs. These properties were studied by Mott Schottky (M-S) analyses (Fig. 8d) through the estimation of charge carrier density (N<sub>d</sub>) and flatband potential (E<sub>fb</sub>) under dark conditions. By plotting the space charge capacitance (C<sub>sc</sub><sup>-2</sup>) in function of the applied potential, a positive slope was achieved in the linear region of plots for all photoanodes. This behaviour is well known for n-type semiconductors, which displays a good accordance with the open circuit response of photoanodes. Accordingly, M-S equation was used to observe the effect of amount of H<sub>3</sub>BO<sub>3</sub> on N<sub>d</sub> and E<sub>fb</sub>:

$$\frac{1}{C_{sc}^2} = \frac{2N_A}{N_d F \varepsilon \varepsilon_0} \left( E_{app} - E_{fb} - \frac{RT}{F} \right)$$
(5)

Where N<sub>A</sub> is the Avogadro's number, F is the Faraday constant,  $\varepsilon_0$  and  $\varepsilon$  are the vacuum and TiO<sub>2</sub> permittivity ( $\varepsilon$  = 50, anatase) respectively, R, the gases constant (8.314 JK<sup>-1</sup> mol<sup>-1</sup>) and E<sub>app</sub> is the potential applied during the measurements. N<sub>d</sub> was estimated from the slope of M-S plots, while the E<sub>fb</sub> was determined from the intercept of the straight line with the potential axis (Table 2). To increase the amount of H<sub>3</sub>BO<sub>3</sub> in the X-BNF-TNTs photoanodes, the achieved positive slope for each material was decreased than that of bare NF-TNTs. The slope diminution in the M-S plots was attributed to a gradual increase of N<sub>d</sub> into the photoanodes. According with the abovementioned XPS Ti 2p analysis, the amount of Ti<sup>3+</sup> were higher after boron modification. Therefore, the increase of N<sub>d</sub> is the direct result of a higher Ti<sup>3+</sup> content after doping. Furthermore, E<sub>fb</sub> was simultaneously displaced to more negative

values, which indicates an increase of accumulated electrons into modified photoanodes.<sup>16,30</sup> In this case, a shift of Fermi level close to CB of TiO<sub>2</sub> was reached. This analysis corroborates the relationship between the PEC performance and the semiconducting properties of X-BNF-TNTs, both influenced by the amount of boron precursor.

**Figure 8.** a) Open-circuit photopotential, b) linear sweep photovoltammetry ( $v = 10 \text{ mV s}^{-1}$ ), c) photocurrent transients (five on/off light cycles) and d) Mott-Schottky analysis under dark conditions for NF-TNTs and X-BNF-TNTs photoanodes, as indicates the figure legends. Electrolyte: 1.0 M Na<sub>2</sub>S (pH 12), illumination: 150 W halide lamp (60 mW cm<sup>-2</sup>).



Dhataanada	M-S parameters			
Photoanode	N <sub>D</sub> 10 <sup>20</sup> / cm <sup>-3</sup>	E <sub>fb</sub> / V vs Ag/AgCl, 3 M KCl		
NF-TNTs	0.63	-0.64		
0.04-BNF-TNTs	1.30	-0.77		
0.06-BNF-TNTs	2.29	-0.82		
0.09-BNF-TNTs	2.72	-0.87		

**Table 2.** Mott-Schottky parameters obtained for NF-TNTs and X-BNF-TNTs photoanodes.

According with the later, the PEC process can describe faithfully the photoresponse of the photoanodes to estimate the adequate preparation conditions. However, to incorporate these types of materials into a photovoltaic device, for instance a QDSSC, two main characteristics should be considered: (1) a transparent photoanode under forward illumination to avoid intensity loss by reverse illumination, and (2) collection a wide amount of low-energy photons to produce a high photocurrent.<sup>12,32,36</sup> In this sense, BNF-TNTs photoanodes were detached from Ti substrate and adhered on ITO. Then, they were sensitized with CdSe QDs using diverse number of SILAR cycles, referred as BNF-Y-CdSe. The PC and PEC properties of prepared photoanodes were measured (Fig. 9) to choose the transparent material with good features (improved light harvesting and electron mobility) to be used in QDSSCs. In addition, the cause of synergism between B-doping and CdSe based sensitizer can be established.

As initial stage, the open circuit potential of free-standing films is shown in Fig. 9a. Before sensitization, the  $E_{oc}$  for bare NF-TNTs membrane was ~-0.82 VA<sub>g/AgCl</sub>, which was a slight less negative than that of free-standing 0.06-BNF-TNTs film~

- 0.85 V<sub>Ag/AgCI</sub>. This corroborated the higher PC performance of BNF-TNTs than that of NF-TNTs observed in Fig. 8. Conversely, the E<sub>oc</sub> of free-standing BNF-TNTs film was displaced towards more negative values to increase the number of SILAR cycles during CdSe QDs sensitization. The estimated E<sub>oc</sub> under photosteady state was ~(-1.10, -1.15, -1.17 and -1.20) V<sub>Ag/AgCI</sub> for 0.06-BNF-Y-CdSe, where Y = 3, 4, 5 and 6 SILAR cycles, respectively. This displacement was attributed to the increase in the number of injected electrons to BNF-TNTs from CdSe QDs, which becomes the Fermi level more negative.<sup>18,28,36,88</sup>

The improvement of light harvesting with the increase of SILAR cycles during CdSe sensitization is also mediated with the decrease of E<sub>g</sub>, requiring less energy to generate more electron-hole pairs and shifts Eoc. Nevertheless, after 450 min under illumination, the BNF-6-CdSe photoanode shows a displacement in the E<sub>oc</sub> to more positive values. This has been claimed that by exceeding the SILAR cycles of CdS and CdSe, an unsuitable band alignment inside the heterostructure can be promoted.<sup>12,19,36</sup> This causes the electron-hole recombination in the composite and decrease its photoresponse. Here, it was demonstrated the Eg narrowing unavoidably provided a closer energy separation between CB positions of TiO<sub>2</sub> and CdSe QDs, which was enough to promote injection electrons to the latter semiconductor. However, the likelihood of carrier recombination increases. To prove this hypothesis, the open circuit potential decay curves (also known as OCPD transient) were achieved from the photopotential decay after interrupting the illumination response of charge carrier recombination as а in the BNF-Y-CdSe/electrolyte interface. The quick or slow response of OCPD is directly proportional to the electron recombination rate. According with the latter, the electron lifetime  $(T_n)$  can be obtained from the reciprocal of potential decay in function of time  $(dE_{oc}/dt)$  by the following relationship (6):<sup>22</sup>

$$\tau_n = -\frac{K_B T}{e} \left(\frac{dE_{oc}}{dt}\right)^{-1} \tag{6}$$

where K<sub>B</sub> is the Boltzmann's constant, T is absolute temperature in K, and e is the electron charge. Fig. 9b depicts the variation of  $\tau_n$  vs potential plots obtained from OCPD transients, showing an increase in electron lifetime by using 5 SILAR cycles upon CdSe sensitization. A high electron lifetime accompanied with a slow OCPD are an indication of high electron recombination resistance mainly associated with the following paths: (1) recombination of accumulated photoelectrons in the CB of CdSe or (2) injected electrons to TiO<sub>2</sub>, with the electrolyte, and (3) electron-hole recombination inside the sensitizer.<sup>88</sup> In this case, it is noteworthy the enhancement of charge carrier recombination inhibition between BNF-Y-CdSe photoanode with the electrolyte (paths 1 and 2), to increase the SILAR cycles to 5. Conversely, by exceeding the SILAR cycles to 6, a fast OCPD and a decrease of  $\tau_n$  were achieved.

Although 6-CdSe QDs injects electrons to BNF-TNTs to generate an increase of  $E_{oc}$  (in all SILAR cycles, the CB of CdSe is higher than BNF-TNTs),  $E_{oc}$  is eventually decreased under illumination (Fig. 9a), indication of electron-hole pair recombination inside the CdSe QDs (path 3). It probes the lowering of CB into the 6-CdSe closer to the BNF-TNTs, causing the photodegradation of CdSe. On the other hand, to analyse the influence of boron doping on the PC properties of BNF-5-CdSe, a bare free-standing NF-TNTs film supported on ITO was also sensitized with 5-CdSe (referred as NF-5-CdSe). A lower  $E_{oc}$  (around 1.02 V<sub>Ag/AgCl</sub>),  $T_n$  and a faster OCPD were obtained unlike the BNF-5-CdSe, which allows to point out that the amount of Ti<sup>3+</sup> formed by the presence of boron is critical for the enhancement of PC response into the composite. The decline of electron recombination in the materials before and after B-doping can be seen to normalize its corresponding OCPD transient and fit the curve with a first-order kinetic model. Then, the recombination rate constant (k<sub>r</sub>) for each photoanode is estimated by the following equation (7):<sup>89</sup>

$$\frac{E - E_{oc}}{E_o - E_{oc}} = 1 - e^{-k_r t}$$
(7)

where E is the potential in any time during the decay,  $E_{oc}$  is the photosteady-state potential and Eo, the steady-state potential under dark. From normalized OCPD transients (inset of Fig. 9b), the recombination rate constants were 5.3 x 10<sup>-2</sup> s<sup>-1</sup> and 1.1 x 10<sup>-2</sup> s<sup>-1</sup> for NF-5-CdSe and BNF-5-CdSe photoanodes, respectively. This indicates the retarding of electron recombination to increase the amount Ti<sup>3+</sup> species and thereby, the electron flow into composite by B-doping. Under illumination conditions, Ti<sup>3+</sup> can donate electrons to the VB of CdSe in the TiO<sub>2</sub>/CdSe heterostructures,<sup>39</sup> which avoids the photodecomposition of sensitizer. Thus, a low kr corroborated the increase of electron lifetime and the PC performance of BNF-5-CdSe after boron incorporation. The charge carrier separation and transport abilities inside the composites were studied by photovoltammetry in positive going direction (Fig. 9c). All cases, the composites generated a higher photocurrent than NF-TNTs and BNF-TNTs.<sup>39,40</sup> This demonstrated the maximizing of visible-light harvesting, the accumulation of more charge carriers, for instance photogenerated holes in the composite to oxidize S<sup>2-</sup> ions from the electrolyte, and the electron transport to back contact upon CdSe sensitization.<sup>29,33</sup>

The latter was corroborated by contact angle measurements, observing an improvement of hydrophilicity in CdSe-sensitized photoanodes than that of bare BNF-TNTs. This indicates an intimate interaction between S<sup>2-</sup> and composite surface (Appx. C). To increase the number of cycles to 5, the highest photocurrent was reached, indication of an efficient spatial separation of photogenerated electron-hole pairs in the TiO<sub>2</sub>/CdSe heterostructure. Conversely, to extend the number of SILAR cycles over 5, the photocurrent was declined, meaning that the charge carrier recombination was favoured. This trend allowed the correlation between photovoltammetry curves with the OCPD transients, to gain understanding about the interaction between BNF-TNTs and CdSe QDs in the heterostructure. According with photopotential measurements for composites, an II-type heterojunction could be established in the TiO<sub>2</sub>/CdSe interface,<sup>22,29,32</sup> providing an increment in the E<sub>oc</sub> to increase the number of SILAR cycles.

**Figure 9.** a) Open circuit photopotential, b) electron lifetime obtained from OCPD and c) linear sweep photovoltammetry ( $v = 10 \text{ mV s}^{-1}$ ) for BNF-Y-CdSe photoanodes. Electrolyte: 1.0 M Na<sub>2</sub>S (pH 12), illumination: 150 W halide lamp (60 mW cm<sup>-2</sup>). Inset of Fig. 9b displays the normalized OCPD of NF-5-CdSe and BNF-5-CdSe photoanodes.



Here, more photogenerated electrons coming from CdSe could be injected to  $TiO_2$  via CB and transported to back contact, which enhances the conducting properties and electron lifetime of composites.<sup>90</sup> Contrariwise, the eventual decrease of  $E_{oc}$  and the quick OCPD to sensitize BNF-TNTs with 6-CdSe, caused the narrowing of CB in the BNF-TNTs/6-CdSe interface. Thus, a minor number of electrons was available

to be transported from the photoanode/electrolyte interface to back contact, decreasing the PEC performance of composites after 6-CdSe sensitization.

The narrowing of CB edges in the BNF-TNTs/CdSe interface by varying the number of SILAR cycles was corroborated through the determination of band structure by using the concept of Millikan electronegativity (Fig. 10). Here, electronegativity of an atom is defined as the average sum of the electron affinity and the ionization potential.<sup>36</sup> According with the latter, the absolute electronegativity ( $\chi$ ) of a semiconductor is the geometric mean of the electronegativity of each atom contained into the material.<sup>47</sup> In this point, the associated energy of CB and VB edges (E<sub>CB</sub> and E<sub>VB</sub>, respectively) can be estimated by equations (8) and (9):<sup>36,91</sup>

$$E_{CB} = \chi - E^e - 0.5E_g \tag{8}$$
$$E_{VB} = E_{CB} + E_g \tag{9}$$

where  $E_e$  is the free energy of electrons in hydrogen scale (4.5 eV).  $\chi_{TiO2}$  and  $\chi_{CdSe}$  were calculated to be 5.80 eV and 4.94 eV, respectively. Calculations of  $E_{CB}$  are often found in the literature at isoelectric point of semiconductors (around 2.0 for Cd chalcogenides and 5.80 for TiO<sub>2</sub>).<sup>38</sup> Nonetheless, to determine the corresponding values at pH 12,  $E_{CB}$  and  $E_{VB}$  were shifted around 0.059 V per pH unit. As seen in Fig. 10, a smaller difference between CB edge of CdSe and BNF-TNTs was achieved to increase the number of SILAR cycles, due to the quantum confinement effect. After 6-CdSe sensitization, the lowest driving force for electron injection from 6-CdSe to BNF-TNTs was generated, which favoured electron-hole pair recombination into the sensitizer. This explains the decrease of photocurrent seen in photovoltammetry curves (Fig. 9c) as response of restrained electron transport to back contact. Further, a much higher photocurrent was produced by BNF-5-CdSe than NF-5-CdSe, consequence of a higher fraction of Ti<sup>3+</sup> in the former material. More electrons can be transferred from Ti<sup>3+</sup> species to CdSe and then to TNTs via CB, improving the PEC properties of BNF-Y-CdSe.

**Figure 10.** Band structure of BNF-Y-CdSe photoanodes in function of number of SILAR cycles (Y).



The charge carrier ability of composites depending on the presence and absence of boron and load of deposited CdSe was also studied by electrochemical impedance spectroscopy (See Appx. D). The corresponding EIS parameters of the materials are summarized in Table D1. Under dark, the lowest electron transport resistance was observed in the BNF-5-CdSe, establishing a suitable band structure to achieve an improved charge carrier separation. By exceeding the number of SILAR cycles, the electron mobility was blocked. Under illumination, the boron modification enhanced the conducting properties of photoanodes, assisting to a higher electron flow to back contact compared with NF-5-CdSe. Results demonstrates the synergism between doping and sensitization to guarantee materials with good PCE.

**4.1.3.** Photovoltaic properties of X-BNF-Y-CdSe composites. By using photoelectrochemistry, it was seen the enhancement of light absorption, charge carrier separation and transport to use the non-metal doping and cadmium selenide sensitization. However, the literature is scarce about the combination of doping and sensitization in phovoltaics, which represents a big challenge the generation of

comparable PCE employing these types of materials, with the conventional cadmium chalcogenides sensitized TiO<sub>2</sub> based photoanodes. In this point, QDSSCs were fabricated by assembling the BNF-5-CdSe composite with a Cu<sub>2</sub>S/Cu cathode, filling the cells with the polysulfide solution. A ZnS layer was deposited on the composite to avoid electron recombination with the electrolyte and its photodecomposition.<sup>19,88</sup>

To validate the synergistic behaviour between B-doping and 5-CdSe sensitization suggested during the electrochemical and PEC characterization, photovoltaic properties of NF-5-CdSe and BNF-5-CdSe photoanodes were investigated through the typical current voltage (J-V) characteristics (Fig. 11a). Photovoltaic parameters as J<sub>sc</sub>, V<sub>oc</sub>, FF and PCE were estimated from the J-V curves and shown in Table 3. As it can be observed, the PCE of BNF-5-CdSe based solar cell was higher than that of NF-5-TNTs one after boron doping. Despite this enhancement, a low Voc and FF were achieved during the measurements. According with literature, the later can be explained by two possible reasons: (1) internal charge carrier recombination inside CdSe QDs or with the polysulfide electrolyte solution, and/or (2) electron trapping by grain boundaries in the CdSe nanoparticle interconnection.<sup>18,88</sup> These issues commonly block carrier transport to the electronic conductor (in this case BNF-TNTs), decreasing the number of available electrons to reach the cathode. In this sense, the electrocatalytic activity of the cathode for regenerating the polysulfide can be decreased. Beyond these disadvantages, a high J<sub>sc</sub> was achieved in the devices, more evidently for the BNF-5-CdSe composite. The increment of Ti<sup>3+</sup> fraction in the BNF-5-CdSe led to improve the sunlight harvesting into the material and assist charge carrier separation into the CdSe more efficiently into a solar device in comparison with the NF-5-CdSe composite.

**Figure 11.** a) Effect of boron on J-V characteristics for composites under 1 sun. Electrolyte: polysulfide solution of 0.5 M Na<sub>2</sub>S + 0.5 M S in DI water: methanol solution (volume ratio 1:1). b) Electron transport mechanism into the CdSe QDs-sensitized BNF-TNTs solar cell.



The highest PCE of champion photoanodes without and with B-doping was 1.07 % and 1.88 %, respectively under 1 sun illumination. The PCE of BNF-5-CdSe was higher than other composite photoanodes reported in the literature, for instance, TiO<sub>2</sub>/CdS/CdSe<sup>12,28</sup> or TiO<sub>2</sub>/CdS<sub>x</sub>Se<sub>1-x</sub><sup>24,25</sup> based heterojunctions. From these results, it was deduced that a photoanode modified by doping/sensitization

combination can be an alternative material in the improvement of PCE in QDSSCs in the future.

According with the optical properties and band structures determined from Millikan approach for composite photoanodes in Fig. 10, an electron transport mechanism into the BNF-5-CdSe/electrolyte interface can be proposed (Fig. 11b). Under illumination, CdSe can generate charge carriers, requiring a band gap of 1.72 eV. Due to the good band alignment formed between BNF-TNTs and CdSe, photogenerated electrons in the sensitizer are injected into the former semiconductor. It facilitates charge carrier separation into CdSe. Simultaneously, N 2p energy levels incorporated into TNTs during anodization process (N-doping) can promote electrons into the CB of TiO<sub>2</sub> by using a band gap of 2.83 eV.<sup>30,74</sup> These levels can also promote electrons to Ti<sup>3+</sup> species requiring 2.36 eV. Ti<sup>3+</sup> are located at 0.47 eV from the bottom of CB. This value is closer than that of energy reported in previous works.<sup>4,6</sup> The matching between Ti<sup>3+</sup> states and VB of CdSe allows an efficient electron transport to the sensitizer, which inhibits charge carrier recombination and photodecomposition of CdSe.<sup>39</sup> By adding boron into the NF-TNTs, more Ti<sup>3+</sup> can be produced, which increases the number of electrons transferred to CdSe. Thus, more electrons can be transported from the BNF-5-CdSe/electrolyte interface to back contact, generating a higher photocurrent (higher PCE) than that of NF-Y-CdSe. Then, electrons are collected by the Cu<sub>2</sub>S/Cu cathode to regenerate the polysulfide solution.

**Table 3.** Solar cell parameters estimated for ZnS layer-covered NF-5-CdSe andBNF-5-CdSe composite photoanodes at 1 sun.

Photoanode	J <sub>sc</sub> / mAcm <sup>-2</sup>	V <sub>oc</sub> / V	FF	PCE / %
NF-5-CdSe	$6.14 \pm 0.46$	$0.43 \pm 0.04$	$0.37 \pm 0.03$	0.98 ± 0.22
Champion*	6.54	0.47	0.35	1.07
BNF-5-CdSe	10.5 ± 0.54	$0.44 \pm 0.01$	$0.36 \pm 0.03$	1.66 ± 0.19

\*QDSSC device with the highest photoconversion efficiency obtained from three samples.

Here, it can be concluded that the effect of boron on the photoelectrochemical properties of BNF-TNTs was studied, finding a direct ratio between the amount of Ti<sup>3+</sup> and the PC/PEC performance of materials. A high amount of Ti<sup>3+</sup> promoted the enhancement of light absorption ability of B-modified materials. The BNF-TNTs adhesion on conducting glass and their CdSe QDs sensitization by SILAR method allowed fabricating semitransparent photoanodes with efficient light harvesting. However, the number of SILAR cycles used during sensitization affected the latter ability, besides of charge carrier separation and transport into the composites. This was caused by band alignment between BNF-TNTs and CdSe QDs, which was suitable after 5 SILAR cycles. An II-type heterojunction structure was formed in the BNF-TNT/5-CdSe interface, facilitating electron injection toward TiO<sub>2</sub>. Thus, a slow OCPD and high electron lifetime in the composite were achieved.

Furthermore, a higher Ti<sup>3+</sup> fraction induced by B-modification enhanced electron flow through BNF-5-CdSe photoanode. It led to generate a PCE of 1.88 %, higher than that undoped composite (1.07 %). The former efficiency was comparable with reported values for other sensitized modified TiO<sub>2</sub> photoanodes. The role of boron into composites allowed to deduce that synergism of doping and chalcogenide sensitization is established by carrier transfer from Ti<sup>3+</sup> donor states into TiO<sub>2</sub> to VB

edge of sensitizer. This favours electron injection and flow into BNF-Y-CdSe/electrolyte interface to reach the back contact.

## 4.2. CdS and CdS/CdS<sub>1-x</sub>Se<sub>x</sub> QDs-sensitized BNF-TNTs photoanodes

4.2.1. Morphology and physicochemical properties of composite photoanodes. Fig. 12 shows typical FESEM top view and cross section images of BNF-TNTs (Fig. 12a,b), after 4-CdS (Fig. 12c,d) and 4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitizations (Fig. 12e,f). Bare BNF-TNTs are compact displaying a pore diameter distribution around 117.3  $\pm$  1.7 nm and wall thickness of 18.5  $\pm$  2.5 nm. Tubes are vertically aligned, showing an average length of 16.6  $\pm$  1.3 µm. After chalcogenide deposition, it was observed the sealing of interspace tube and the presence of nanoparticles along the tubular structure and the top of pores. The average pore size and wall thickness were decreased to be 107.1  $\pm$  2.5 nm and 35.0  $\pm$  4.1 nm for the BNF-4-CdS composite, respectively. For the BNF-4-CdS-5-CdS1-xSex, its corresponding values were 96.3  $\pm$  5.9 nm and 60.5  $\pm$  9.1 nm, respectively. This indicates that large pores facilitated the penetration of the Cd<sup>2+</sup>, S<sup>2-</sup> and Se<sup>2-</sup> alcohol SILAR precursors into the inner and outer side of TNTs.<sup>69</sup>

A well-covered surface in each composite was obtained, which benefits the enhancement of the light harvesting capability in the materials. Furthermore, a smaller pore size was achieved for the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composite than that of BNF-4-CdS, which is the evidence of a higher number of nanoparticles deposited on the composites after the 5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitization.

**Figure 12.** FESEM images of top-view and cross-section of a,b) BNF-TNTs, c,d) 4-CdS and e,f) 4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> photoanodes.



Fig. 13 shows representative TEM images of the BNF-4-CdS and BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> (Fig. 13a,b). The tubular structure was observed for both the composites besides the presence of sensitizer nanoparticles covering the TNTs. This indicates the complete deposition of CdS and CdS<sub>1-x</sub>Se<sub>x</sub> nanoparticles along the tubes after chalcogenides sensitization. Black zones were observed on the composite surfaces, which was attributed to well-dispersed nanoparticles on the

BNF-TNTs. Nevertheless, a higher amount of those black zones was achieved for the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>, as result of the deposition of more nanoparticles after ternary alloy sensitization. This agrees with the morphology analyzed by FESEM for this material.

As seen in Fig. 13c,d, HR-TEM images displays the preferential planes of the CdS and CdS<sub>1-x</sub>Se<sub>x</sub> covering the BNF-TNTs. The interplanar spacing of 0.35 nm, was associated with the (101) plane from anatase phase (PDF-21-1272 from ICDD),<sup>12</sup> while the lattice fringe around 0.20 nm and 0.22 nm corresponded to the (110) and (220) planes from CdS.<sup>92,93</sup> The anatase phase and the (110) plane from CdS were found in both the composites. In addition, interplanar distances around 0.31 nm and 0.36 nm were ascribed to the (101) and (100) planes from CdS into CdS<sub>1-x</sub>Se<sub>x</sub>.<sup>42,94</sup> Nanoparticle sizes of the chalcogenides covering the BNF-TNTs were also estimated to be around 7.85 ± 0.11 nm and 5.59 ± 0.30 nm for CdS and CdS<sub>1-x</sub>Se<sub>x</sub>, respectively. These values indicated the QD-scale of the sensitizers. The distribution and co-existence of chalcogenides on BNF-TNTs were also observed by STEM-mapping and Raman spectroscopy (Appx. E).

**Figure 13.** Typical TEM images of a) BNF-4-CdS and b) BNF-4-CdS-CdS<sub>1-x</sub>Se<sub>x</sub> composites. c,d) HR-TEM image of materials.



Changes in the optical properties of BNF-Y-CdS and BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites were studied through the diffuse reflectance spectra, where their bandgap (E<sub>g</sub>) values were estimated by the modified Kubelka-Munk approach (Fig. 14). Bare BNF-TNTs showed two slopes associated with two different E<sub>g</sub> values (Fig. 14a). Both the E<sub>g</sub> were lower than intrinsic E<sub>g</sub> of TiO<sub>2</sub> (3.2 eV), indicating the presence of intra band gap energy levels. The photoactivation energies at 2.80 eV and 2.31 eV were ascribed to the electron transitions from N 2p energy levels to CB of TiO<sub>2</sub>, and Ti<sup>3+</sup> donor species formed by substitutional fluorine/interstitial boron into semiconductor, respectively.<sup>51,80</sup> From the latter energies, it was deduced that Ti<sup>3+</sup> is located at 0.49 eV from the CB edge of TiO<sub>2</sub>.<sup>30</sup> B, N and F atoms can be introduced into the TiO<sub>2</sub> lattice during the BNF-TNTs growth, promoting the B,N,F-codoped of TiO<sub>2</sub>.

On the other hand, to increase the number of SILAR cycles (Y) during CdS sensitization (Fig. 14a), a red shift in the E<sub>g</sub> value was achieved. This indicated a lower energy to generate electron excitations in the chalcogenide. Eg values were estimated to be (2.25, 2.20, 2.16 and 2.13) eV for Y-CdS, where Y = 3, 4, 5 and 6 SILAR cycles, respectively. Furthermore, it has been claimed that Eg,bulk of CdS is around 2.42 eV.<sup>36</sup> However, the deposition of Y-CdS on BNF-TNTs provided lower Eg values than that of CdS bulk. It meant that the optical properties of BNF-Y-CdS composites did not depend on the particle size (quantum confinement effect), but the amount of CdS deposited SILAR cycle by cycle. It could be explained in terms of adsorbed Cd<sup>2+</sup> excess on the CdS after SILAR sensitization. This has been claimed that during the SILAR process, an excess of unreacted Cd<sup>2+</sup> is remained on CdS surface. The adjacent cations on the CdS surface can promote the formation of Cd-Cd bonds in the nanoparticle interconnection, also considered as interfacial states located close to the VB edge of chalcogenide.  $^{51,52}$  The lowering of  $E_g$  to increase the SILAR cycles suggested the formation of more Cd-Cd energy levels, upward shifting the VB edge closer to the CB into the CdS.

After 5-CdS<sub>1-x</sub>Se<sub>x</sub> deposition as outer sensitizer on the BNF-4-CdS composites, modified K-M curves were obtained as shown in Fig. 14b. To increase the Se content in the ternary alloy,  $E_g$  values were red-shifted than those CdS composites. This indicated the narrowing of  $E_g$  by tuning the band edges of CdS with Se addition, which produced the CdS<sub>1-x</sub>Se<sub>x</sub> alloy formation.  $E_g$  values were determined to be (1.87, 1.82, 1.78 and 1.67) eV for CdS<sub>1-x</sub>Se<sub>x</sub> with S/Se molar ratio = 2.0, 1.0, 0.5 and 0, respectively. The decrease of  $E_g$  in the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites was accompanied with a change in the coloration of materials from light to dark red. Here, the ternary sensitizes showed characteristics of binary CdS (yellow) and CdSe (brownish red) to vary the Se content (Fig. 14c). A high Se fraction into the CdS<sub>1-x</sub>Se<sub>x</sub>

meant that its optical properties were increasingly similar than that CdSe. The formation of CdS<sub>1-x</sub>Se<sub>x</sub> alloys was corroborated by their corresponding  $E_g$ , which was in intermediate values between  $E_{g,bulk}$  of CdS<sup>48</sup> and CdSe.<sup>21,35</sup>

**Figure 14.** Kubelka-Munk approach for  $E_g$  estimation in a) BNF-Y-CdS and b) BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> photoanodes. c) Photograph of the 4-CdS and 4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>-sensitized BNF-TNTs varying the S/Se molar ratio in the ternary alloys.



The chemical composition and environment of BNF-TNTs before and after 4-CdS and 5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitizations were investigated by XPS analysis, as shown in Fig. 4. From survey spectrum (Fig. 15a), the presence of Ti, C, O, Cd and S was verified in the BNF-4-CdS composite, while Se was also observed in the BNF-4-CdS/5-CdS<sub>1-x</sub>Se<sub>x</sub>. Ti signal was decreased after sensitization. B, N and F were not detected in the materials, indicating the low content of these elements. According with the latter, high resolution XPS (HR-XPS) spectra of B 1s, N 1s, F 1s,

and Ti 2p were also achieved (Appx. F). HR-XPS N 2p spectrum displays 3 peaks at 397.6, 399.7 and 402.8 eV. These peaks were attributed to the substitutional (N-Ti-N and N-Ti-O bonds) and interstitial N (N-O-Ti bonds) or NO<sub>x</sub> adsorbed on BNF-TNTs, respectively.<sup>30,95</sup> F 1s peak was also showed at 684.1 eV, associated to substitutional F into TiO<sub>2</sub>.<sup>30,80</sup> B 1s spectrum provided an unique peak at 190.5 eV, ascribed to the interstitial boron (B-O-Ti bonds) into TiO<sub>2</sub>.<sup>16,46</sup> The incorporation of substitutional F/interstitial B affected the chemical species of Ti, observed in the Ti 2p spectrum. Peaks at 458 and 463.6 eV corresponded to Ti<sup>4+</sup> species from TiO<sub>2</sub>, while peaks achieved at 455.8 and 461.2 eV were attributed to Ti<sup>3+</sup> species.<sup>16,30,80</sup> A doublet observed at 460 and 465.3 eV was ascribed to Ti-F, according with the assigned contribution in the F 1s spectrum.<sup>57</sup> These results confirmed the B, N, F-co-doping of TNTs after anodization.

Fig. 15b depicted the HR-XPS Cd 3d spectra of the BNF-TNTs after 4-CdS and 5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitization. Both the composites showed main doublets at 404.8 and 411.6 eV, corresponding to Cd  $3d_{5/2}$  and Cd  $3d_{3/2}$  signals from the cadmium cations into the CdS. However, each Cd 3d peak was decomposed in two additional contributions. First doublet at 404.9/411.5 eV was endorsed to Cd-S bond from chalcogenides, while the second doublet at 406.5/413.2 eV was attributed to Cd-Cd energy states in the CdS and CdS<sub>1-x</sub>Se<sub>x</sub> nanoparticles.<sup>52,96</sup> This has been claimed that the Cd-Cd energy levels are composed by Cd 5s electrons. These electrons are far away from Cd core requiring a high binding energy to be detected.<sup>52</sup> The peak identification reinforced the idea about why E<sub>g</sub> values for the BNF-Y-CdS are lower than that of CdS bulk, discussed above: the higher the amount of Cd-Cd energy states, the higher the upward shifting of the CdS VB, leading to a narrowed E<sub>g</sub>.

In the case of  $CdS_{1-x}Se_x$ , the influence of Cd-Cd energy levels into a ternary alloy prepared by SILAR has not been explained in the literature. Nonetheless, Comparing the determined  $E_g$  of both the CdS- and CdS<sub>1-x</sub>Se<sub>x</sub>-sensitized materials by K-M approach, we suggested that Cd-Cd energy levels do not affect in a high proportion

the optical properties of the latter photoanodes, due to the formed energy levels by Se modification ( $E_g < 2.0 \text{ eV}$ ). Even so, the presence of these states can influence other properties of composites (for instance, electron transport to back contact). Lastly, N was also achieved in the Cd 3d spectrum for 4-CdS at 402.7 eV, come from adsorbed NO<sub>x</sub> on BNF-TNTs surface.<sup>30</sup>

**Figure 15.** a) XPS survey and HR-XPS b) Cd 3d, c) S 2p and d) Se 3d spectra of BNF-TNTs before and after 4-CdS and 5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitizations.



Fig. 15c exhibited the S 2p spectra of both the Cd chalcogenides composites, where two doublets were attained from S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks. The first doublet at 161.4/163.6 eV was related with the sulfide anions in the CdS,<sup>96,97</sup> while the doublet at 168.2/169.4 eV was ascribed to the SO<sub>3</sub> species on CdS shell.<sup>98</sup> The latter

contribution was shifted around 1.0 eV for the 5-CdS<sub>1-x</sub>Se<sub>x</sub>, assigned to the SO<sub>4</sub>.<sup>97-99</sup> This indicated the partial oxidation of the CdS and CdS<sub>1-x</sub>Se<sub>x</sub> surfaces, which is unavoidable even in ultrahigh vacuum conditions.<sup>99</sup> For BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub>, an additional doublet appeared at 159.3/165.2eV, corresponding to Se 3p signals from Se into the outer sensitizer.<sup>22</sup> The existence of Se in the 5-CdS<sub>1-x</sub>Se<sub>x</sub> was also corroborated by the Se 3d spectrum (Fig. 15d), achieving a typical doublet at 53.7/54.8 eV.<sup>21,92</sup>

4.2.2. Photo(electro)chemical and photovoltaic properties of BNF-Y-CdS composites. The photochemical (PC) performance of free-standing BNF-TNTs films sensitized with CdS QDs by varying the SILAR cycles was observed by photopotential measurements (Fig. 16). Upon illumination, the photopotential of all composites, denoted as E<sub>oc</sub>, was displaced to more negative values (Fig. 16a), which was attributed to the n-type semiconductivity of composites. The  $E_{oc}$  values of BNF-Y-CdS were (-1.03, -1.12, -1.10, and -0.87) V<sub>Ag/AgCl</sub> for Y = 3, 4, 5, and 6 SILAR cycles, respectively. The E<sub>oc</sub> of bare BNF-TNTs was -0.82 V<sub>Ag/AgCI</sub>. It means that the CdS sensitization improved light harvesting of TiO<sub>2</sub>. By comparing the E<sub>oc</sub> values of the composites, the higher the number of SILAR cycles to 4, the higher the E<sub>oc</sub> was reached, improving the electron injection and accumulation in the CB of BNF-TNTs. This promoted the Fermi level shift of  $TiO_2$  closer to its CB. However, the  $E_{oc}$  was decreased by exceeding the SILAR cycles over 4. According with the K-M approach (Fig. 13a), the Eg of CdS QDs was narrowed to increase the number of SILAR cycles due to the introduction of Cd-Cd energy states close to the VB of chalcogenide.<sup>51,52</sup> In this case, a low Eg value was obtained due to an upward shift of VB, providing a closer energy separation with the energy levels of TiO<sub>2</sub>.

The displacement of E<sub>oc</sub> to less negative values after depositing 5-CdS and 6-CdS QDs was ascribed to the formation of Cd-Cd energy levels excess into composites, which facilitated charge carrier recombination in the sensitizer and the decrease of PC response of composites. The presence of Cd-Cd energy levels was achieved by

turning off the illumination, where two shoulders (denominated as P<sub>1</sub> and P<sub>2</sub>) appeared during open circuit potential decay (OCPD). This indicated the presence of two diverse species on the composite surface after a PC oxidation process. Cd-Cd energy levels are composed by residual Cd<sup>2+</sup> from CdS surface, favouring the adsorption of sulfur-containing anions. Accordingly, the electrolyte nature is composed by sulfide (S<sup>2-</sup>) and sulphite (SO<sub>3</sub><sup>2-</sup>) anions, which act as sacrificial reagent to enhance the photostability of BNF-Y-CdS. This means that the latter species can be adsorbed and oxidized in the photoanode/electrolyte interface transferring electrons to CdS. The oxidation process of sulfide and sulphite anions is carried out through the following reactions (10) and (11):<sup>86,96</sup>

$$2S^{2-} + 2h^+ \to S_2^{2-} \tag{10}$$

$$SO_3^{2-} + S^{2-} + 2h^+ \to S_2O_3^{2-} \tag{11}$$

A stabilized  $E_{oc}$  under photosteady state was obtained after two light on/off cycles, avoiding the photodecomposition of CdS QDs. P<sub>1</sub> and P<sub>2</sub> signals were ascribed to adsorbed S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and S<sub>2</sub><sup>2-</sup> anions, respectively. To corroborate the peak assignation, photopotential measurements were conducted by using the BNF-4-CdS in an electrolyte composed by S<sup>2-</sup> anions. Here, the P<sub>2</sub> signal was only achieved. The magnitude of P<sub>1</sub> and P<sub>2</sub> peaks was increased to elevate the number of SILAR cycles to 4. The high E<sub>oc</sub> in the BNF-4-CdS also indicated (1) the increase of Cd<sup>2+</sup> to react with sulfur species and (2) the generation of more available photoholes to increase the oxidizing power of composite to carry out the reactions 10 and 11. Furthermore, This has been claimed the generation of S<sup>--</sup> radicals from direct reaction of S<sup>2-</sup> anions and the photogenerated holes in chalcogenides (reaction 12). These radicals rapidly react with other sulfide anions to produce polysulfide radicals, denoted as (S<sub>n+1</sub>)<sup>--</sup>. Then, (S<sub>n+1</sub>)<sup>--</sup> species (reaction 13):<sup>33</sup>

$$S^{-.} + nS^{2-} \to (S_{n+1})^{-.}$$
 (12)
$$(S_{n+1})^{-} + Y - CdS(e^{-}) \to (S_{n+1})^{2-} + Y - CdS$$
 (13)

The presence of sulfur species suggests the formation of sulfide/sulphite radicals in the photoanode/electrolyte interface and their subsequent reactions (equations 12 and 13), not only with other anions in solution, but also with  $S^{2-}$  anions from CdS. This is supported for the OCPDs, where  $P_1$  and  $P_2$  peaks were eventually more pronounced after each light on/off cycle. This indicates the adsorption of more sulfur species on the photoanode surface.

The preparation of Cd-chalcogenide-sensitized free-standing films adhered on transparent conducting substrates maximize the light harvesting and their transformation at electricity, 10,26,45 which also depends mainly on the load of deposited sensitizer. For this case, the fabrication of photovoltaic devices using the BNF-Y-CdS photoanodes allowed estimate the material with the best photovoltaic properties in function of the number of SILAR cycles during CdS sensitization. In this sense, typical J-V performance curves were achieved for the BNF-Y-CdS photoanodes, assembling each material to a CuS/FTO cathode and filling the devices with the polysulfide solution. To avoid the carrier recombination between the BNF-TNTs and Y-CdS QDs, with the electrolyte, two ZnS layers were deposited on the composite surface.<sup>12,45</sup> As seen from Fig. 16b, both the J<sub>sc</sub>, V<sub>oc</sub> and FF estimated from the J-V curves were increased after the deposition of 4-CdS on the BNF-TNTs. Conversely, the sensitization of bare BNF-TNTs with 5-CdS and 6-CdS QDs led to the decrease of Jsc and Voc. The photovoltaic parameters extracted from the J-V curves are shown in Table 4. An efficient electron injection occurs from 4-CdS to BNF-TNTs via CB and then transferred to the back contact, increasing the photocurrent generated by the device.<sup>90</sup>

Furthermore,  $V_{oc}$  depends on the number of accumulated electrons in BNF-TNTs. This photovoltaic parameter is defined as the difference between the quasi-Fermi Level and the energy associated to the redox couple used as electrolyte (S<sup>2-</sup>/Sn<sup>2-</sup>).<sup>75</sup> The higher electron content in the composite, the higher V<sub>oc</sub> value is achieved. After 5-CdS sensitization, the decrease of PCE was twofold: (1) by exceeding the load of CdS QDs over 4, a higher number of nanoparticles was deposited on BNF-TNTs surface, providing more recombination sites by Cd-Cd energy levels in the composites. (2) The use of conventional CuS/FTO cathode which loss eventually its performance to electrocatalyze the polysulfide redox reactions by removing the CuS film. After assembling the BNF-4-CdS photoanode with a Cu<sub>2</sub>S/Cu cathode, a higher J<sub>sc</sub> and FF were achieved, indication of an improved polysulfide solution renovation. As seen in Appx. G, the Cu<sub>2</sub>S/Cu shows higher stability than CuS/FTO after photovoltaics process, which can be caused by the reaction of free Cu and the polysulfide solution. This avoids the loss of electrocativity in the Cu-cathode.

The PCE of device using the Cu<sub>2</sub>S/Cu was around 0.76 %, while a maximum efficiency of 0.46 % was reached to use CuS/FTO cathode. On the other hand, the synergistic effect between boron-doping and CdS sensitization was studied to compare the photovoltaic performance of composites in presence and absence of dopant. This also allowed to determine the nature of energy levels affecting charge carrier transport in the BNF-TNTs/CdS interface. A higher J<sub>sc</sub> and V<sub>oc</sub> were obtained for BNF-4-CdS than those CdS-sensitized TiO<sub>2</sub> nanotubes without B-doping (NF-4-CdS), due to an increase of Ti<sup>3+</sup> species by the presence of boron. According with the XPS analysis, the fraction of Ti<sup>3+</sup> (located at 0.49 eV from CB of TiO<sub>2</sub>) was increased after B-doping (from 1.23 to 1.72 %), which represents more transported electrons into the composite.<sup>16,45</sup> Ti<sup>3+</sup> can transfer electrons to CdS, promoting charge carrier separation and the increase of photocurrent in the device.<sup>39</sup> The PCE of NF-4-CdS by using the Cu<sub>2</sub>S/Cu cathode was around 0.38 %. Hence, the improvement of electron-hole pair separation and transport into BNF-TNTs/CdS interface was reached.

**Figure 16.** a) Open circuit photopotential, b) J-V performance characteristics  $(v = 50 \text{ mV s}^{-1})$  and c) Schematic representation of band structure into the BNF-Y-CdS photoanodes in function of number of SILAR cycles (Y). Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination source: halide lamp (60 mW cm<sup>-2</sup>). The J-V measurements were conducted under simulated solar light (100 mWcm<sup>-2</sup>) in 0.5 M Na<sub>2</sub>S + 0.5 M S in DI water: methanol solution (volume ratio 1:1).



 Table 4. Solar cell parameters estimated for ZnS layer-covered BNF-Y-CdS

 composite photoanodes at 1 sun.

Photoanode	J <sub>sc</sub> / mAcm <sup>-2</sup>	V <sub>oc</sub> / V	FF	PCE / %
BNF-TNTs/FTO	$0.47 \pm 0.07$	$0.14 \pm 0.02$	$0.16 \pm 0.08$	0.01 ± 3x10 <sup>-3</sup>
Champion*	0.42	0.12	0.18	0.01
3-CdS/FTO	2.10 ± 0.07	$0.26 \pm 0.02$	$0.34 \pm 0.03$	$0.19 \pm 0.04$
Champion*	2.17	0.28	0.36	0.22
4-CdS/FTO	3.86 ± 0.06	$0.40 \pm 0.03$	$0.25 \pm 0.04$	$0.38 \pm 0.07$
Champion*	3.93	0.42	0.28	0.46
5-CdS/FTO	3.68 ± 0.19	0.37 ± 0.01	0.31 ± 0.01	0.41 ± 0.02
Champion*	3.89	0.37	0.30	0.43
6-CdS/FTO	$3.45 \pm 0.34$	0.26 ± 0.01	$0.29 \pm 0.02$	$0.26 \pm 0.02$
Champion*	3.78	0.26	0.27	0.27
NF-4-CdS/Cu <sub>2</sub> S	2.82 ± 0.30	$0.34 \pm 0.02$	$0.37 \pm 0.04$	$0.36 \pm 0.02$
Champion*	3.16	0.36	0.33	0.38
BNF-4-CdS/Cu <sub>2</sub> S	5.04 ± 0.13	$0.42 \pm 0.01$	$0.37 \pm 0.01$	$0.70 \pm 0.08$
Champion*	5.15	0.42	0.35	0.76

\*QDSSC device with the highest photoconversion efficiency obtained from three samples.

The spatial charge carrier separation and transport abilities of BNF-Y-CdS composites were also seen by electrochemical Impedance spectroscopy (EIS) through Nyquist plots (Appx. H, Fig. H1). EIS parameters are depict in Table H1. After 4-CdS sensitization, the lowest electron mobility resistance was achieved as result of favoured electron injection from 4-CdS to BNF-TNTs mediated by Cd-Cd energy levels.

The band structure modification of BNF-Y-CdS by varying the SILAR cycles during sensitization process was achieved (Fig. 16c), estimating their corresponding conduction and valence band edges using the equations (8) and (9):<sup>36,91</sup>

$$E_{CB} = \chi - E^e - 0.5E_g$$
(8)  
$$E_{VB} = E_{CB} + E_g$$
(9)

where E<sub>CB</sub> and E<sub>VB</sub> are the conduction and valence energy levels,  $\chi$  is the absolute electronegativity of semiconductors (5.80 eV and 5.07 eV for TiO<sub>2</sub> and CdS, respectively), and E<sup>e</sup>, the free energy of electrons in the solid (4.5 eV).  $\chi$  was calculated from geometric mean of Millikan electronegativities of the elements contained in the oxide and chalcogenide.<sup>91</sup> In order to obtain the band structure at pH 12, E<sub>CB</sub> and E<sub>VB</sub> were displaced 0.059 V per pH unit, considering that isoelectric point pH of CdS and TiO<sub>2</sub> are around 2.0 and 5.8, respectively.<sup>38</sup> Although the quantum confinement effect is not validated for chalcogenides where their respective E<sub>g</sub> < E<sub>g,bulk</sub>, the incorporation of intra band-gap levels into sensitizer is the key factor to decrease E<sub>g</sub>. In the case of CdS, low photoactivation energy is caused by the introduction of Cd-Cd levels, upward shifting the VB of chalcogenide.<sup>51,52</sup> To increase the number of SILAR cycles to 4 during CdS sensitization, a balance between E<sub>g</sub> and an adequate band alignment between Ti<sup>3+</sup> and Cd-Cd levels is achieved.

By exceeding the number of SILAR cycles over 4, more intra band gap Cd-Cd states are added, trapping electrons in the grain boundaries to hinder their transport to back contact. In addition, the driving force between Ti<sup>3+</sup> to Cd-Cd energy levels for electron transport is decreased, contributing to carrier recombination in the BNF-Y-CdS composite. This can explain low phovoltaic parameter values (Table 4) and a high carrier transport resistance into BNF-5-CdS and BNF-6-CdS materials.

**4.2.3.** Photo(electro)chemical and photovoltaic properties of BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites. After choosing the suitable number of SILAR cycles of Y-CdS QDs to promote a suitable way for photogenerated carrier transport in a photovoltaic device, ternary alloys based on 5-CdS<sub>1-x</sub>Se<sub>x</sub> QDs were deposited on the BNF-4-CdS surface. This was carried out to overlap the limited low-energy harvesting provided by 4-CdS ( $E_g = 2.20 \text{ eV}$ ), transport more charge carriers to the back contact and improve the PCE in QDSSCs. As a first approach, photopotential measurements were conducted on BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites (Fig. 17), where the PC response of the materials mainly depended on the different nominal S/Se molar ratios in the ternary alloy (Fig. 17a).

The n-type semiconducting behaviour was observed in all composites by shifting the  $E_{oc}$  to negative values upon illumination. According with the n-type characteristic of CdS, an II-type heterostructure in the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interface can be established. The photo-steady  $E_{oc}$  values were determined to be (0.86, 1.09, and -0.93) V<sub>Ag/AgCI</sub> for the photoanodes with S/Se molar ratios about 2.0, 1.0, 0.5, respectively. A cosensitized BNF-4-CdS-5-CdSe was also studied by comparative purposes, obtaining the lowest  $E_{oc}$  around -0.77 V<sub>Ag/AgCI</sub>. To decrease the S/Se molar ratio to 1.0 in the ternary sensitizer, the  $E_{oc}$  value was displaced to more negative potentials, which indicated the enhancement of light harvesting, the photogeneration and accumulation of more charge carriers in the heterostructure.

However, the lower the S/Se molar ratio, more positive  $E_{oc}$  was. It has been claimed to vary of S/Se molar ratio in CdS<sub>1-x</sub>Se<sub>x</sub> sensitized TiO<sub>2</sub> photoanodes, the VB and CB edges of the ternary alloy can be tuned to match with the band edges of TiO<sub>2</sub> or a co-sensitizer.<sup>22-25</sup> Here, the higher the amount of Se in the CdS<sub>1-x</sub>Se<sub>x</sub>, the lower the E<sub>g</sub> and the energy difference between the CB edges of ternary chalcogenide and the TiO<sub>2</sub>/CdS were. A cascade-type structure could be produced into the composite, which facilitated electron injection from the CdS<sub>1-x</sub>Se<sub>x</sub>/electrolyte interface to BNF-TNTs mediated by CdS.<sup>22,26</sup> Therefore, an adequate band alignment in the BNF-TNTs/CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interfaces was achieved for a S/Se molar ratio = 1.0, to promote carrier separation. Conversely, by exceeding the Se content in the ternary alloy (S/Se < 0.5), a lower driving force could be developed in the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> heterojunction, inducing charge carrier recombination and generation of a low E<sub>oc</sub>. To corroborate electronic transfer ability from CdS<sub>1-x</sub>Se<sub>x</sub> to CdS in each composite, open circuit decay (OCPD) curves were observed after turning off the illumination. A fast/slow OCPD is proportional to carrier recombination rate in the materials. The electron lifetime ( $\tau_n$ ) of CdS/CdS<sub>1-x</sub>Se<sub>x</sub> heterojunction can be estimated from the reciprocal of the OCPD by the following relationship (6):<sup>24</sup>

$$\tau_n = -\frac{K_B T}{e} \left(\frac{dE_{oc}}{dt}\right)^{-1} \tag{6}$$

where K<sub>B</sub> was denoted as Boltzmann's constant, e as the electron charge, T as the absolute temperature and  $(dE_{oc}/dt)^{-1}$ , the reciprocal of photopotential decay under dark. By plotting T<sub>n</sub> vs potential decay (Fig. 17b), it was observed that an increase of T<sub>n</sub> and a slow OCPD were reached to decrease the S/Se molar ratio to 1.0, which was an indication of a high electron recombination resistance into the co-sensitizers heterostructure. A smaller S/Se molar ratio promoted a faster OCPD and a decrease of T<sub>n</sub>, due to a declined electron-hole pair separation in the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interface. It probes that the S/Se molar ratio in the ternary sensitizer affected the heterojunction established between the co-sensitizers, providing a poor alignment by increasing the Se content. Here, the photogenerated electrons in the CB of CdS<sub>1-x</sub>Se<sub>x</sub> can recombine with the holes accumulated in the VB or with the oxidized species from the electrolyte.<sup>23,24,26</sup> On the other hand, some works have reported high sunlight harvesting capability and photovoltaic efficiency of CdS/CdSe co-sensitized TiO<sub>2</sub> based photoanodes in QDSSCs.<sup>12,21,45</sup>

Even so, by obtaining a typical open-circuit response of a BNF-4-CdS-5-CdSe composite, the lowest  $E_{oc}$ ,  $T_n$ , and the fastest OCPD were achieved. This indicated

a deficient electron transfer and a high charge carrier recombination rate in the CdS/CdSe interface. Electron recombination rates ( $k_r$ ) for each photoanode were estimated to normalize their corresponding OCPD curves and fit the decay to a first-order model (7):<sup>72</sup>

$$\frac{E - E_{oc}}{E_o - E_{oc}} = 1 - e^{-k_r t}$$
(7)

where E was the potential measured during the OCPD,  $E_0$  was denoted as the potential under steady state conditions and  $E_{oc}$  was the photosteady-state potential. From the normalized OCPD curves shown in the inset of Fig. 6b, the  $k_r$  values were calculated to be  $3.2 \times 10^{-2} \text{ s}^{-1}$ ,  $4.8 \times 10^{-3} \text{ s}^{-1}$ ,  $3.1 \times 10^{-2} \text{ s}^{-1}$  and  $5.2 \times 10^{-1} \text{ s}^{-1}$  for the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites with S/Se = 2.0, 1.0 and 0.5, respectively. The suitable cascade-type structure formed into the BNF-TNTs/CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interfaces for S/Se = 1.0 led to a better electron-hole pair separation in the ternary sensitizer than those the other chalcogenide ratios, which retarded charge carrier recombination in the heterostructure.<sup>22</sup> More holes are available in the VB of CdS<sub>1-x</sub>Se<sub>x</sub> to react with the electrolyte and avoid the photodecomposition of sensitizer.

The S/Se molar ratio in the outer CdS<sub>1-x</sub>Se<sub>x</sub> sensitizer defines, not only low-energy absorption capability in the harvester, but also the charge carrier mobility from CdS<sub>1-x</sub>Se<sub>x</sub>/electrolyte interface to the back contact. The latter two characteristic are essential for an efficient performance in a QDSSC. To study the photovoltaic properties of the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites, each material was assembled to a Cu<sub>2</sub>S/Cu cathode and filled with the polysulfide solution consisted of S<sup>2-</sup>/Sn<sup>2-</sup> methanol/water solution. J-V performance curves were obtained (Fig. 17d), where the photovoltaic parameters as J<sub>sc</sub>, V<sub>oc</sub> and FF were extracted and shown in Table 5. The PCE of the QDSSCs using each material was estimed from the photovoltaic parameters. A similar V<sub>oc</sub> was obtained for the photoanodes with

S/Se = 2.0 and 1.0, which means an effective electron injection from the CdS<sub>1-x</sub>Se<sub>x</sub> to BNF-TNTs, displacing the quasi-Fermi level close its CB.<sup>16,30</sup>

**Figure 17.** a) Open circuit photopotential, b) electron lifetime from photopotential decay and c) J-V performance characteristics ( $v = 100 \text{ mVs}^{-1}$ ) of the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> photoanodes. Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination source: halide lamp (60 mWcm<sup>-2</sup>). The J-V measurements were conducted under simulated solar light (100 mWcm<sup>-2</sup>) in 0.5 M Na<sub>2</sub>S + 0.5 M S in DI water: methanol solution (volume ratio 1:1). Inset of Fig. 17b show the normalized photopotential decay.



Nevertheless, J<sub>sc</sub> and FF were higher in the latter S/Se molar ratio. A higher Se content in the ternary alloy led to a narrowing of the E<sub>g</sub>, improving visible-light harvesting to generate more charge carrier in the composite. This modification could cause indirectly a low-energy difference between CB edges in the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interface. Even so, this change was enough to promote the formation of a cascade-type structure in the heterojunction to increase electron flow into harvester.<sup>15,18</sup> Accumulated holes in the outer sensitizer can react with the polysulfide solution to renew the electrons transported to the back contact. PCE values were around 1.71 % and 2.58 % for composites by using the 5-CdS<sub>0.67</sub>Se<sub>0.33</sub> and 5-CdS<sub>0.50</sub>Se<sub>0.50</sub>, respectively. The latter value is higher than those other devices by using outer ternary alloys as sensitizers in QDSSCs.<sup>10,24,26</sup>

**Table 5.** Solar cell parameters estimated for ZnS layer-coveredBNF-4-CdS-5-CdS1-xSex composite photoanodes at 1 sun.

Photoanode	J <sub>sc</sub> / mAcm <sup>-2</sup>	V <sub>oc</sub> / V	FF	PCE / %
5-CdS <sub>0.67</sub> Se <sub>0.33</sub>	$9.56 \pm 0.60$	$0.47 \pm 0.02$	$0.36 \pm 0.06$	$1.60 \pm 0.17$
Champion*	10.13	0.47	0.36	1.71
5-CdS <sub>0.50</sub> Se <sub>0.50</sub>	14.10 ± 0.55	0.45 ± 0.01	$0.40 \pm 0.01$	2.51 ± 0.10
Champion*	14.36	0.45	0.40	2.58
5-CdS <sub>0.33</sub> Se <sub>0.67</sub>	12.98 ± 0.45	$0.35 \pm 0.02$	$0.32 \pm 0.04$	1.45 ± 0.19
Champion*	12.74	0.36	0.36	1.65
5-CdSe	$11.49 \pm 0.44$	0.36 ± 0.01	0.29 ± 0.01	1.17 ± 0.09
Champion*	11 28	0.27	0.20	1 26

\*QDSSC device with the highest photoconversion efficiency obtained from three samples.

By exceeding the amount of Se in CdS<sub>1-x</sub>Se<sub>x</sub> to S/Se < 0.5,  $J_{sc}$ ,  $V_{oc}$  and FF were declined, indication of a low electron to the back contact. In this case, a narrowed  $E_g$  was obtained, increasing the harvested photons by the ternary sensitizer. However,

a low V<sub>oc</sub> indicated that less electrons were injected to the BNF-TNTs mediated by CdS, shifting the Fermi level to more positive potentials. This meant that the CB band edge of CdS exhibited a similar o higher energy than that of CdS<sub>1-x</sub>Se<sub>x</sub>, which restrains carrier mobility into the heterostrcture.<sup>22-24,26</sup> The electron-hole pair recombination is facilitated in the CdS<sub>1-x</sub>Se<sub>x</sub>/electrolyte interface, which could provide the photodissolution of ternary alloy. Thus, the PCE for the BNF-4-CdS-5-CdS<sub>0.33</sub>Se<sub>0.67</sub> was decreased to 1.65 %. The 5-CdSe-sensitized photoanode achieved the lowest PCE around 1.26 %.

By comparing the V<sub>oc</sub> of the latter material and the BNF-4-CdS studied under the same experimental conditions (Table 4), a lower voltage value was obtained in presence of the ternary alloy. The photovoltaic measurements agree with the opencircuit response of each material. Furthermore, through EIS spectra (Appx. H, Fig. H2) obtained for composites by varying the added Se content into ternary alloy, a facile pathway for electron transport was obtained for S/Se = 1.0. This corroborates the formation of an adequate band alignment to avoid charge carrier recombination and enhance the conducting properties of composites, to achieve a high PCE.<sup>32</sup> EIS parameters of CdS<sub>1-x</sub>Se<sub>x</sub>-senstized materials are shown in Table H2.

Similar for BNF-4-CdS materials, a complex band structure of BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites was deduced to corroborate the band edge variation to modify the amount of added Se into ternary alloy (Fig. 18). Here,  $E_{VB}$  were achieved by obtaining normalized XPS VB spectra for BNF-TNTs, BNF-4-CdS and BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> (Appx. I), where their corresponding values were estimated through extrapolation method.  $E_{VB}$  values (in eV scale) were converted to potential scale (vs Ag/AgCl,  $V_{Ag/AgCl}$ ) by applying a modified equation (14):<sup>100</sup>

$$V_{Ag/AgCl} = \phi + E_{VB} - E^e - 0.21 V \tag{14}$$

where,  $\phi$  is the work function of the analyzer (4.33 eV). On basis of these results, E<sub>CB</sub> edges were determined from equation (9). As seen in Fig. 18, the E<sub>VB</sub> of 4-CdS was around 0.46 V<sub>Ag/AgCI</sub>, which was lower than that the value obtained from electronegativity approach (equation 8) around 0.76 V<sub>Ag/AgCI</sub>. The difference around 0.3 V between both the latter band edge values was attributed to estimation method. The spectroscopical approach (equation 14) considers the Fermi level alignment in formed heterojunctions, while the former is applied for individual semiconductors and theoretical values are achieved. Nonetheless, the matching tendency in the BNF-TNTs/CdS interface is suitable to use both the calculations. This is the main issue in CB and VB edges determination in this kind of systems.

**Figure 18.** Band structure into the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> photoanodes in function of Se content into ternary alloy, obtained from XPS VB.



By increasing the Se content into  $CdS_{1-x}Se_x$ ,  $E_{CB}$  becomes eventually more positive, decreasing the energy difference with  $E_{CB}$  of CdS. Even so, this value is already more negative than that of CdS to promote the electron injection. This corroborates the improved photovoltaic properties of analyzed materials by band engineering. In

addition, a mismatch in the 4-CdS/5-CdSe heterojunction is established, which explains the lowest photo(electro)chemical and photovoltaic performance of this composite. According with the latter band structure, the influence of the Se incorporation on the photoconversion ability can be explained by proposing an electron transfer mechanism in a binary/ternary co-sensitizer assembling (Fig. 19). For a S/Se = 2.0, a high energetic difference between the CB edge of CdS and CdS<sub>1-x</sub>Se<sub>x</sub> is recognized. However, the highest photoactivation energy is required to generate electron-hole pairs. When Se content reaches a S/Se = 1.0, a balance between carrier photogeneration and their transport to the current collector is established, favouring the highest electron lifetime and the lowest k<sub>r</sub>. Thus, the best photo(electro)chemical and photovoltaic performance were achieved. In the case of the S/Se = 0.5, the lowest  $E_g$  is observed to harvest a high number of low-energy photons. Even so, an unsuitable band structure is generated for electron transport.

Lastly, some reports about the beneficial<sup>12,21,45</sup> or detrimental<sup>22,32,48</sup> effect of CdS/CdSe co-sensitization on the photovoltaic performance of a QDSSCs exhibit disparate views. Here, CdSe generates electrons to be transported to CdS via Cd-Cd energy levels. Even so, CdS can also transfer electrons to the CdSe via CB. This explains the lowest electron lifetime and highest k<sub>r</sub> estimed for BNF-4-CdS-5-CdSe, due to an inhibited charge carrier separation and transport. Further, as it was seen in the XPS section, Cd-Cd energy levels were also identified into ternary alloys sensitized materials prepared by SILAR, which can act as recombination centers in the nanoparticle grain boundaries. The latter contributes to the detriment of overall carrier flow to the back contact. This can be considered as one of the main causes to obtain lower PCEs values than that reported for ternary cadmium chalcogenides sensitized solar cells around 7-11 %.<sup>3,42,101</sup> Nonetheless, as an initial step, it is vital to recognize what are the key features of the composites as band structure, formed energy levels, etc., that influence directly on PCE.

In conclusion, since preparation of chalcogenide sensitized photoanodes by SILAR method, Cd-Cd energy levels are generated into sensitizers, modifying the optical, photo(electro)chemical and photovoltaic properties of the composites. The amount of these energy levels is varied to change the load of CdS QDs deposited on the BNF-TNTs, affecting the visible-light absorption and charge carrier transport abilities into the BNF-TNTs/CdS/electrolyte interface. The highest PCE around 0.76 % was achieved in a QDSSC to use the BNF-4-CdS composite, because of a direct carrier transfer between Ti<sup>3+</sup> and a suitable Cd-Cd energy level content into the photomaterial. Therefore, the later energy levels control the carrier transport capability of composites.

Furthermore, the deposition of Se-rich ternary sensitizers allowed to reach a balance between low-energy light harvesting and adequate band structure in the 4-CdS/5-CdS<sub>1-x</sub>Se<sub>x</sub> interface, for a S/Se molar ratio = 1.0. A cascade type-heterojunction promoted carrier mobility from the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interface to the BNF-TNTs. Therefore, the highest  $E_{oc}$ ,  $T_n$  and the lowest electron recombination rate were obtained. The PCE of BNF-4-CdS-5-CdS<sub>0.50</sub>Se<sub>0.50</sub> under 1 sun conditions was around 2.58 %. An excess of Se in the ternary alloy caused a mismatch into the 4-CdS/5-CdS<sub>1-x</sub>Se<sub>x</sub> interface, declining the photovoltaic performance of QDSSCs.

**Figure 19.** Charge carrier separation and transport mechanism from CdS/CdS<sub>1-x</sub>Se<sub>x</sub> to BNF-TNTs tailoring the band edges of the outer sensitizer to vary the S/Se molar ratio.



## 4.3. Mn-CdS and Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> QDs-sensitized BNF-TNTs photoanodes

4.3.1. Morphological and physicochemical characterization of composites. Fig. 20 depicts the FESEM images of the BNF-TNTs photoanodes before (Fig. 20a,b) and after the deposition of inner 0.7-Mn-CdS (Fig. 20c,d) and outer  $2-Bi_2S_3$  (Fig. 20e,f), where the top-view and cross section of the material surface were observed. BNF-TNTs were vertically oriented, showing cavities with an average diameter around  $116.6 \pm 2.6$  nm. The width of the cavities was decreased after the deposition of sensitizer nanoparticles, achieving an increase of the wall thickness in the tubular structure. Furthermore, it is seen that the sensitizers were also deposited along the nanotubes, covering the nanotube interspace. The BNF-0.7-Mn-4-CdS before and after Bi<sub>2</sub>S<sub>3</sub> sensitization exhibited a pore diameter distribution around 94.6 ± 5.0 nm and 84.3 ± 7.1 nm, respectively. An average BNF-TNTs length around  $16.7 \pm 1.0$  nm was achieved. Here, alcoholic cationic and anionic SILAR solutions can percolate large cavities and lengths in nanotubular structures, considering the low surface tension of the solvent, which produces a wellcover surface.<sup>69</sup> The presence of the sensitizers on the BNF-TNTs surface is essential to produce a red shift in the visible-light absorption of  $TiO_2$ , to harvest a high number of low-energy photons.

**Figure 20.** Top-view and cross-section FESEM images of a,b) BNF-TNTs, c,d) 0.7-Mn-CdS and e,f) 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> photoanodes.



To observe the distribution of the sensitizers-based nanoparticles and their corresponding sizes, TEM and HR-TEM images were obtained for the BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite (Fig. 21). As seen at low magnification

(Fig. 21a) the co-sensitizer nanoparticles covered all the entire nanotube structure, forming a well-dispersed decorate. To enlarge the magnification (Fig. 21b), the nanotube interspacing was sealed by the sensitizer deposition, which is in good agreement with the FESEM images. In addition, the ZnS layer was seen to cover the nanoparticles, providing a protect effect. This is the main characteristic of ZnS to avoid the direct contact with the electrolyte solution to promote the carrier recombination and thereby, the loss of PCE in a photovoltaic device.<sup>21,55</sup> On the other hand, HR-TEM was achieved for the composite, where different preferential planes were observed on the material surface (Fig. 21c). The interplanar spacing around 0.35 nm was ascribed to the (101) plane from anatase phase in the BNF-TNTs,<sup>12</sup> while the corresponding lattice fringes at 0.34 nm and 0.37 nm were attributed to the (111) plane from CdS and (002) plane from Bi<sub>2</sub>S<sub>3</sub>.<sup>102,103</sup> Lastly, the sizes of Mn-CdS and Bi<sub>2</sub>S<sub>3</sub> nanoparticles were determined to be 7.76 ± 0.15 nm and 7.20 ± 0.21 nm, respectively. This indicates the formation of QDs based sensitizers.

For verifying the presence of each deposited sensitizer on the BNF-TNTs surface, Raman spectra were achieved before and after co-sensitization (Fig. 21d). For a bare BNF-TNTs, five representative peaks at (143.6, 192.6, 391.4, 514.4 and 633.8) cm<sup>-1</sup> were observed, corresponding to the anatase phase. However, after sensitization, the anatase peaks were diminished and diverse new peaks appeared depending on the sensitizer nature. After Mn-CdS sensitization, two peaks were obtained at 296.7 and 595 cm<sup>-1</sup>, associated to the LO phonons in the CdS.<sup>104</sup> Apparent changes were not seen after Bi<sub>2</sub>S<sub>3</sub> deposition due to the excitation energy of Raman laser (532 nm) is closer to the band gap of CdS bulk (2.42 eV) than that the Bi<sub>2</sub>S<sub>3</sub> (1.2-1.7 eV). Nonetheless, after decomposing the peak around 292 cm<sup>-1</sup> for BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>, three new signals were achieved at 244, 261.5 and 291.1 cm<sup>-1</sup>. First and second peaks were associated to the LO phonons of Bi<sub>2</sub>S<sub>3</sub> and the third one was attributed to the LO phonon from CdS.<sup>104,105</sup> Here, the formation of each chalcogenide during SILAR sensitization of BNF-TNTs was corroborated. **Figure 21.** a) Typical TEM image of BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite, b) Large magnification and c) HR-TEM image of composite. d) Raman spectra of BNF-TNTs before and after Mn-CdS and  $Bi_2S_3$  sensitizations. The anatase (A) signals are depicted in the Raman spectra.



Optical properties of BNF-TNTs before and after 0.7-Mn-CdS and 2-Bi<sub>2</sub>S<sub>3</sub> sensitizations (Fig. 22) were observed by achieving the corresponding band gap (E<sub>g</sub>) values in modified Kubelka-Munk (K-M) curves (Fig. 22a). CdS-sensitized BNF-TNTs (BNF-CdS) was also prepared for comparative purposes. Bare BNF-TNTs displayed two red-shifted E<sub>g</sub> at 2.87 eV and 2.36 eV, which differs from the intrinsic value of TiO<sub>2</sub> (3.2 eV). This indicates the presence of intra band gap energy states into TiO<sub>2</sub>. Latter values were attributed to N 2p $\rightarrow$ CB and N 2p $\rightarrow$ Ti<sup>3+</sup> electron

transitions, respectively.<sup>30,80</sup> The generation of Ti<sup>3+</sup> into TNTs was carried out by F and B incorporation, enhancing the visible-light absorption of photoanode.<sup>14,30</sup>

After CdS sensitization by SILAR, the Eg of composite was lowered to 2.27 eV, which means the improvement of its visible-light harvesting. According with the obtained E<sub>g</sub>, the quantum confinement effect was not achieved for this material due to this value is lower than that of CdS bulk (2.42 eV). The energy variation has been associated to the generation of intra band gap energy levels into chalcogenide when SILAR method is used to deposit CdS quantum dot-based nanoparticles.<sup>51</sup> During sensitization, residual Cd<sup>2+</sup> is retained on the CdS nanoparticle surface, forming sulfur vacancies. The subsequent nanoparticle deposition forms Cd-clusters or also known as Cd-Cd energy levels, upward shifting the VB of CdS (See Appx. J).<sup>51,52</sup> Here, electronic transitions from occupied Cd 5s ( $\sigma$ ) bonding orbital to unoccupied Cd 5s ( $\sigma^*$ ) antibonding orbital are carried out.<sup>52</sup> Furthermore, by incorporating Mn into CdS, a red-shift in Eg of chalcogenide was reached again to be around 2.16 eV. Several works about Mn-doped CdS base materials have mentioned that Mn<sup>2+</sup> states are located close to the CB of CdS, causing the decrease of its photoactivation energy.<sup>55,63-65,67</sup> Considering the latter structural changes provided by SILAR method and Mn-modification, band gap of 2.16 eV in the Mn-doped CdS was ascribed to the electron transitions from Cd-Cd energy states to Mn<sup>2+</sup> energy levels.

After depositing Bi<sub>2</sub>S<sub>3</sub> on the BNF-TNTs/CdS and BNF-TNTs/Mn-CdS surfaces, the light absorption of composites was again red-shifted to 1.41 and 1.32 eV, respectively, which was accompanied with an increase in the F(R) function. It meant a high extinction coefficient from Bi<sub>2</sub>S<sub>3</sub> to photogenerate charge carriers. For this chalcogenide, it has been reported that the estimated Bulk E<sub>g</sub> (E<sub>g,bulk</sub>) is around 1.2-1.7 eV,<sup>56,57</sup> corroborating the formation of Bi<sub>2</sub>S<sub>3</sub> quantum dot nanoparticles. Despite this feature, the E<sub>g</sub> of outer Bi<sub>2</sub>S<sub>3</sub> decreases to be deposited on the Mn-CdS. The literature is scarce to explain this kind of E<sub>g</sub>-modification after co-sensitization.

However, the reason of these discrepancy can be attributed to indirect electronic transition from VB of  $Bi_2S_3$  to  $Mn^{2+}$  states into Mn-CdS (Fig. 22b).

**Figure 22.** a) Modified K-M spectra of the BNF-TNTs before and after CdS and  $Bi_2S_3$  sensitizations, in presence and absence of  $Mn^{2+}$  b) schematic representation of electronic transitions into BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> material according with K-M approach.



observing the chemical and species the By state contained in BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite, XPS analyses were performed (Fig. 23). Survey spectra of BNF-0.7-Mn-4-CdS before and after 2-Bi<sub>2</sub>S<sub>3</sub> sensitization were achieved, where main elements as Cd, Mn, S and Bi were identified (Fig. 23a). The chemical environment of BNF-TNTs was not seen in the latter spectra of sensitized samples, deducing that the analysis provided information about the surface of chalcogenides deposited on BNF-TNTs. In this way, survey spectrum and highresolution (HR) XPS spectra of the elements conforming the bare BNF-TNTs were also obtained, noting the presence of diverse species associated to B, N, F and Ti as representative elements in the sample (Appx. K). Considering the decomposition of the characteristic signals of each element into BNF-TNTs, species like substitutional N and F and interstitial boron were found. Furthermore, the signal of

Ti<sup>3+</sup> is depicted in the HR-XPS Ti 2p, formed by the co-existence of B and F into TiO<sub>2</sub> lattice.<sup>14,30,80</sup> These results support the B, N, F-co-doping of TiO<sub>2</sub> nanotubes, promoted during Ti anodization.

Fig. 23b shows the typical HR-XPS Cd 3d spectra for BNF-0.7-Mn-4-CdS before and after Bi<sub>2</sub>S<sub>3</sub> sensitization, which exhibit two main peaks around 405/411.7 eV. These signals are ascribed to the Cd  $3d_{5/2}$  and Cd  $3d_{3/2}$  doublet of CdS. Nonetheless, the former photoanode contains other two complement Cd 3d doublet at 405.8/412.5 eV, associated to the Cd-Cd bonding into Cd-chalcogenide. This type of interaction can be detected at high binding energies due to the bond is composed by the electrons that belong to the Cd 5s orbitals.<sup>51,52</sup> This assignation corroborates the suggestion of the E<sub>g</sub> narrowing in CdS for obtaining lower values than that of CdS bulk during SILAR sensitization. Therefore, the optical properties of Mn-CdS does not depends on the particle size, but the added intra band gap levels during its preparation. On the other hand, after Bi<sub>2</sub>S<sub>3</sub> sensitization Cd-Cd energy states were not observed in the composite, suggesting the reaction of excess Cd<sup>2+</sup> with S<sup>2-</sup> during Bi<sub>2</sub>S<sub>3</sub> deposition.

The decomposition of HR-XPS Mn 2p spectrum of composite without bismuth sulfide shows representative four peaks (Fig. 23c). Peaks at 618.8/653.4 eV corresponded to Cd 3p<sub>3/2</sub> and Cd 3p<sub>1/2</sub> in the CdS, while the contributions centered at 642.2 eV and 645.8 eV were assigned to Mn 2p<sub>3/2</sub> and Mn<sup>2+</sup> satellite, respectively. This indicates the presence of divalent Mn<sup>2+</sup> within a CdS matrix. <sup>64,106</sup> According with relative sensitivity factors, the amount of Mn doping CdS into three different BNF-X-Mn-CdS composites were estimated to be 0.6, 0.7, and 1.0 at.%. (named hereafter as 0.6-Mn-CdS, 0.7-Mn-CdS and 1.0-Mn-CdS). The low amount of Mn indicates that doping modification was reached. However, the intensity of Cd 3p<sub>1/2</sub> and Mn contributions in the Mn 2p spectrum of BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> was decreased, deducing that Bi-chalcogenide shields the element identification.

In addition, The Bi<sub>2</sub>S<sub>3</sub> sensitizer was identified by comparing the HR-XPS S 2p for the abovementioned composites. In both the materials, S 2p spectra shows two peaks at 161/162.1 eV, that in the case of BNF-TNTs/Mn-CdS, was ascribed to S<sup>2-</sup> anions from CdS (Fig. K2). The doublet centered at 167.7/169.2 eV was associated to the presence of SO<sub>x</sub>, indicating the partial oxidation of Mn-CdS surface.<sup>107</sup> Conversely, for Mn-modified CdS, the former peaks co-exist with the main Bi 4f doublet at 158.2/163.5 eV, in a typical Bi 4f + S 2p overlapped spectra of Bi<sub>2</sub>S<sub>3</sub> (Fig. 23d).<sup>107,108</sup> SO<sub>x</sub> species were not appeared after Bi<sub>2</sub>S<sub>3</sub> sensitization, which indicates the inhibition of composite oxidation.

**Figure 23.** a) XPS survey and HR-XPS b) Cd 3d, overlapped c) Mn 2p + Cd 3p and d) Bi 4f + S 2p spectra of BNF-TNTs after 0.7-Mn-CdS and 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> sensitizations.



4.3.2. Photo(electro)chemical, semiconducting and photovoltaic properties of BNF-X-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>. To favour an efficient electron flow from the Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interface to BNF-TNTs, a suitable number of SILAR cycles during BNF-Mn-Y-CdS sensitization was estimated by photoelectrochemical measurements (Fig. 24). As seen in Fig. 24a, the highest photocurrent was achieved for the BNF-Mn-4-CdS, indication of an assisted electron-hole pair separation and mobility into the composite. However, the photocurrent of composite decayed for BNF-Mn-5-CdS, response of the blocked charge carrier mobility. According with the K-M approach and XPS Cd 3d spectrum, light harvesting ability of chalcogenides was not affected by particle size changes (there was not quantum confinement effect), due to E<sub>g</sub> of CdS and Mn-CdS were lower than E<sub>g,bulk</sub>. Here, optical properties were influenced by the incorporation of intraband gap Cd-Cd energy levels into Mn-CdS during sensitization. These states are close to the VB of chalcogenide.<sup>51,52</sup> Thus, the higher the Cd-Cd energy level content to increase the SILAR cycles, the higher the upward shift of Mn-CdS VB. Simultaneously, more Mn<sup>2+</sup> energy levels close to the CB of doped material can be introduced, providing a red-shift of band gap compared with CdS. A downshift of CB by Mn<sup>2+</sup> states can cause a poor band alignment with BNF-TNTs, which decreases electron injection capability and favours carrier recombination into Mn-CdS.64,65,67

To corroborate the charge carrier transport ability of the sensitized photoanodes, photocurrent transient measurements were carried out under 5 light on/off cycles at 0  $V_{Ag/AgCl}$  (Fig. 24b). Once the illumination is turned on, a quick photocurrent is generated as result of the spatial separation and transport of charge carriers.<sup>105</sup> After light is turned off, the photocurrent decays with presence of tails. This indicates that some electrons are trapped into sensitizer blocking its returning to VB.<sup>109</sup> In this case, BNF-Mn-3-CdS and BNF-Mn-4-CdS composites showed a constant steady-state photocurrent during each cycle, ensuring high stability and good charge carrier transport. It is well known that S<sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> redox solution acts like sacrificial agent to avoid the photodecomposition of chalcogenides.<sup>67,105</sup> Nevertheless, the

BNF-Mn-5-CdS exhibited a slow increase of photocurrent during each transient. This is a clear behaviour of the restrained electron injection from Mn-CdS to BNF-TNTs via CB. The latter is also reflected in the lowest generated photocurrent.

**Figure 24.** a) Photovoltammetry ( $v = 10 \text{ mV s}^{-1}$ ) and b) photocurrent transient measurements (five on/off light cycles) for BNF-Mn-Y-CdS composites. c) Schematic representation of electron transportation ability of materials in function of number of SILAR cycles (Y) during Mn-CdS sensitization. Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination: 150 W halide lamp (60 mW cm<sup>-2</sup>).



Considering the latter result, another explanation of electron transport depending on the number of SILAR cycles is the amount of sensitizer nanoparticles deposited on BNF-TNTs. As is shown in Fig. 24c, the nanoparticle interconnection generates grain boundaries, where the photogenerated electrons can be trapped, restraining their transport to back contact.<sup>87</sup> Thus, the higher the number of SILAR cycles, the higher the amount of grain boundaries could be formed into composite, promoting electron recombination in the Mn-CdS/electrolyte interface.<sup>10</sup>

Similar for the suitable load of deposited sensitizer on the BNF-TNTs surface, the amount of Mn<sup>2+</sup> was also essential to promote an adequate band structure for the electron transport into the BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite (Fig. 25). Here, photocurrent transients were performed, applying a bias potential of 0 V<sub>Ag/AgCl</sub> under 5 light on/off cycles. The electron transfer ability into co-sensitized materials was observed by varying the Mn<sup>2+</sup> content into CdS. Unlike of the photoanodes in absence of Bi<sub>2</sub>S<sub>3</sub>, the co-sensitization generates more pronounced tails in the chronoamperometric curves after turn off the illumination, indication of a trap-mediated carrier recombination into the composites.<sup>109,110</sup> it is noteworthy the increase of nanoparticle content after Bi<sub>2</sub>S<sub>3</sub> deposition, which produces more grain boundaries to harm charge carrier separation and mobility.<sup>59,60</sup> This can be the main reason to explain the low photocurrent and energy conversion of Bi<sub>2</sub>S<sub>3</sub> based solar cells.

Even so, the generated steady-state photocurrent by the composite with the lowest Mn<sup>2+</sup> content into CdS (BNF-0.6-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>) was higher than those of BNF-0.6-Mn-CdS composites (Fig. 25a), which indicates doped sensitizer acts like a bridge for the injected electrons from Bi<sub>2</sub>S<sub>3</sub>. Despite this improvement, the bridgefeature of Mn-CdS is influenced by its Mn<sup>2+</sup> content. By increasing the amount of Mn from 0.6 to 0.7 at. %, the highest photocurrent was obtained in the composite, which attributed to the formation of an II-type heterojunction was into BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>. The incorporation of an adequate amount of Mn<sup>2+</sup> generates energy levels closer to CB of CdS, decreasing its energetic difference with the CB edge of BNF-TNTs.<sup>63-65</sup> Nevertheless, the Mn<sup>2+</sup> states can also mediate the

electron injection from Bi<sub>2</sub>S<sub>3</sub>/electrolyte interface to be transported to the back contact. Conversely, by exceeding the Mn content to 1.0 at%, a detriment in the photocurrent was recognized (around 1.8 times). A poor band alignment is generated in the BNF-1.0-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> interface, favouring carrier recombination into inner chalcogenide.

In the case of BNF-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>, the generated photocurrent was lower than that of BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>, which was attributed to a narrow difference between CB edge in the CdS/Bi<sub>2</sub>S<sub>3</sub> interface, restraining the electron mobility to BNF-TNTs. Here, Bi<sub>2</sub>S<sub>3</sub> can inject electrons to CdS via intraband gap energy levels, which can promote electrons to the CB of chalcogenide. The low driving force produced in the chalcogenide interface enables charge carrier recombination into Bi<sub>2</sub>S<sub>3</sub>, decreasing its photoelectrochemical performance. Works about benefit<sup>8,21,111</sup> or detriment<sup>22,48,62,112</sup> about using binary couples type structures in photovoltaic cells are diverse.

Even so, the results demonstrate that the band structure of this kind of systems limits carrier flow in the devices. The incorporation of  $Mn^{2+}$  species into CdS sensitizer allowed to generate an adequate pathway for electron transport from outer  $Bi_2S_3$  to BNF-TNTs. Thus, it is noteworthy that the semiconducting properties of inner CdS were also modified by the presence of  $Mn^{2+}$ . Changes in the band structure into the BNF-TNT/Y-Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> composites were studied by Mott-Schottky (M-S) analysis under dark conditions (Fig. 25b). The charge carrier density (N<sub>d</sub>) and flatband potential ( $E_{fb}$ ) were determined in function of the amount of added  $Mn^{2+}$  into the CdS. For all photoanodes, the space charge capacitance ( $C_{sc}^{-2}$ ) in function of the applied potential ( $E_{app}$ ) was plotted, obtaining a positive slope. This was an indication of the n-type semiconducting behaviour of materials.

**Figure 25.** a) Photocurrent transient measurements (five on/off light cycles) and b) Mott-Schottky (M-S) analysis under dark conditions for BNF-X-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> photoanodes in function of number amount of Mn (X). c) Flat-band ( $E_{fb}$ ) lowering in the composites by increasing Mn<sup>2+</sup> content into CdS. Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination source: halide lamp (60 mWcm<sup>-2</sup>).



According with the latter, the M-S equation was used to estimate the  $N_d$  and  $E_{fb}$  (Table 6) for each composite (5):

$$C_{SC}^{2-} = \frac{2N_A}{N_d F \varepsilon \varepsilon_0} \left( E_{app} - E_{fb} - \frac{RT}{F} \right)$$
(5)

where N<sub>A</sub> and F were the Avogadro's number and Faraday constant, while  $\varepsilon_0$  and  $\varepsilon$ were the vacuum and the corresponding CdS permittivity ( $\epsilon = 8.9$ ). R was denoted as the gases constant. All photoanodes depicts a positive slope, meaning the n-n type heterostructure formed in the CdS/Bi<sub>2</sub>S<sub>3</sub> and X-Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interfaces. On the other hand, by adding Mn during CdS modification, a progressive increase of Nd and a lower E<sub>fb</sub> were reached for the composites. This trend can be explained in terms of the influence of Mn<sup>2+</sup> states on the associated energy to Fermi level of each material. It has been reported that in Mn-doped CdS structures, Mn<sup>2+</sup> are located into the band gap of the CdS, close to its CB edge.<sup>63</sup> By increasing the amount of Mn, discrete Mn<sup>2+</sup> energy levels can produce a continuous level into the chalcogenide (Fig. 25c). Therefore, the higher the Mn<sup>2+</sup> fraction into the CdS, the more positive the E<sub>fb</sub> value is, indicating a change in the Fermi level displaced close to a lower CB minimum.<sup>67</sup> This explains the narrowing of band-gap energy of the BNF-X-Mn-4-CdS photoanode compared with an Mn<sup>2+-</sup>absent BNF-4-CdS material. A lowered CB edge into the Mn-CdS can promote a suitable band alignment with Bi<sub>2</sub>S<sub>3</sub> to boost electron transport capability of BNF-X-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite.

**Table 6.** Mott-Schottky parameters obtained for BNF-X-Mn-4-CdS composite photoanodes after  $Bi_2S_3$  deposition.

Dh	otoppado	M-S parameters		
FI	oloanoue	N <sub>D</sub> 10 <sup>21</sup> / cm <sup>-3</sup>	E <sub>fb</sub> / V vs Ag/AgCl, 3 M KCl	
	CdS	1.83	-0.62	
0.6	-Mn-CdS	2.91	-0.40	
0.7	′-Mn-CdS	4.29	-0.35	
1.0	-Mn-CdS	5.10	-0.16	

Another approach to probe the band structure modification of the composites after Mn<sup>2+</sup> incorporation is through determination their photochemical performance (Fig. 26). Open circuit photopotential (E<sub>oc</sub>) of both the BNF-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> and BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> photoanodes (or simply  $4-CdS-2-Bi_2S_3$ and 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>, respectively) was measured after obtaining a steady state potential under dark (Fig. 26a). Upon illumination, their corresponding potentials were shifted to more negative values, which is a typical response of n-type materials. This corroborates the observed semiconducting behaviour in the abovementioned M-S plots. E<sub>oc</sub> of 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> and 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> were estimated to be -0.61 V<sub>Ag/AgCl</sub> and -0.71 V<sub>Ag/AgCl</sub>, respectively. A higher E<sub>oc</sub> in the Mn-modified composite is the indication of an enhanced electron accumulation, promoted by a facile transport in the Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interface.

The latter can be achieved by the availability of  $Mn^{2+}$  to receive injected electrons from CB of CdS, avoiding carrier recombination with the VB of each sensitizer or the electrolyte solution.<sup>55,63,64</sup> In addition, the presence of  $Mn^{2+}$  states below the bottom of CB from CdS narrows its E<sub>g</sub>, requiring low energy-photons to carry out the electronic transitions into composite. The E<sub>g</sub> narrowing causes a good band alignment in the Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interface provided by the lowering of CB in the Mndoped chalcogenide.<sup>65,67</sup> To verify the charge carrier separation capability into photoanodes in presence of Mn<sup>2+</sup> states, open circuit potential decay (OCPD) was obtained by interrupting the illumination. The rate of the potential relaxing is associated to the facilitated/hindered electron-hole recombination process. From OCPD curves, the electron lifetime (Tn) was determined to use the reciprocal of the OCPD (dE<sub>oc</sub>/dt) by considering this equation (6):<sup>87</sup>

$$\tau_n = -\frac{K_B T}{e} \left(\frac{dE_{oc}}{dt}\right)^{-1} \tag{6}$$

where K<sub>B</sub>, T and e were the Boltzmann's constant, absolute temperature in K, and electron charge, respectively. By plotting Tn vs relaxing potential extracted from OCPD curves (Fig. 26b), it was achieved a higher electron lifetime and a slower OCPD in 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> than that 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite. This represented the adequate II-type heterostructure formed into the former material by the Mn<sup>2+</sup> incorporation, resulting in an enhancement of charge carrier recombination resistance. Although the carrier recombination is highly enabled into 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>, the generation of  $E_{oc}$  indicates that  $Bi_2S_3$  can inject electrons to CdS not only via CB, but also through intraband gap energy levels. Cd-Cd energy states closer to the VB of CdS can collect the electrons where then they are excited to its CB. In a I-type band alignment, electrons are flow back to Bi<sub>2</sub>S<sub>3</sub>, accelerating the quenching of the photochemical response of material.<sup>22,48</sup> According with the latter, a high electron lifetime is the main characteristic for an efficient light-current energy conversion in a photoanode. Electron recombination rates  $(k_r)$  with and without Mn-doping in the composites were calculated to normalize the open circuit potential decay and fit the curve to a one order equation (7):<sup>70</sup>

$$\frac{E - E_{oc}}{E_o - E_{oc}} = 1 - e^{-k_r t}$$
(7)

where E was the relaxing potential under dark,  $E_0$  and  $E_{oc}$  were denoted as the potential under steady state conditions under dark and light conditions, respectively. From the inset of Fig. 26b, the k<sub>r</sub> value for the 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> was calculated to be  $1.1 \times 10^{-2} \text{ s}^{-1}$ , while for 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> was around 2.6 x  $10^{-3} \text{ s}^{-1}$ . The retarding of electron-hole pair recombination does not only ensure an efficient electron mobility into the heterostructures, but also a prolonged stability of sensitizers. The lowering of electron transport resistance into the composites by the presence of  $Mn^{2+}$  was also studied by electrochemical impedance spectroscopy (EIS), through Nyquist plots (Appx. L). EIS parameters are depict in Table L1. A smaller semicurve for Mn-modified composite represents than that of unmodified

material represents a facile electron pathway from Bi<sub>2</sub>S<sub>3</sub> to back contact mediated by Mn<sup>2+</sup> states, increasing the conducting properties in the former photoanode.<sup>63,67</sup>

**Figure 26.** a) Photopotential, b) Electron lifetime decay and c) J-V performance characteristics ( $v = 100 \text{ mVs}^{-1}$ ) of the 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> and 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites. Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination source: halide lamp (60 mWcm<sup>-2</sup>). The J-V curves were conducted under simulated solar light (100 mWcm<sup>-2</sup>) in 0.5 M Na<sub>2</sub>S + 0.5 M S in DI water: methanol solution (volume ratio 1:1). Inset of Fig. 26b shows the normalized photopotential decay.



The main factor for obtaining a good PCE in QDSSCs is the use of photoanodes with improved light harvesting and charge carrier transportation abilities. By photoelectrochemistry, it was observed the enhancement of the latter features in the BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites by Mn<sup>2+</sup> introduction. Nonetheless, the PCE is still a huge challenge in this kind of devices, due to some narrow-band gap sensitizers can collect a lot of photons to produce carriers in a wide spectral region, but they are not able to flow these carriers into the device. This is the case of Bi<sub>2</sub>S<sub>3</sub> sensitized TiO<sub>2</sub> based materials, where a low driving force for electrons are generated in the TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> interface. Thus, PCEs lower than 1.0 % have been reached.<sup>58-61,113</sup> By adding an inner sensitizer to form an adequate band structure, the electrons can be efficiently transported to the back contact, increasing the PCE of a solar cell.

To contribute to the enhancement of PCE of Bi<sub>2</sub>S<sub>3</sub>-sensitized solar cells, the photovoltaic performance of 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite with the best photoelectrochemical properties was studied (Fig. 26c). The photoanode composed by 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> was also analysed to understand the effect of Mn<sup>2+</sup> states on the PCE. Composites were assembled with a Cu<sub>2</sub>S/Cu cathode and filled with the S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup> methanol polysulfide solution. The corresponding current-voltage (J-V) curves were achieved, extracting the photovoltaic parameters as J<sub>sc</sub>, V<sub>oc</sub>, and FF to calculate the PCE of devices (Table 7). V<sub>oc</sub> and J<sub>sc</sub> for the 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> was higher than that of 4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>, which means that BNF-TNTs accumulate more injected electrons from the Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interface than that of CdS/Bi<sub>2</sub>S<sub>3</sub>.<sup>63,66</sup> The electron collection displaces the quasi Fermi level of BNF-TNTs close to its CB,<sup>67</sup> transferring more carriers to the back contact.

The Mn<sup>2+</sup> states into CdS change the CdS/Bi<sub>2</sub>S<sub>3</sub> heterojunction from I-type to II-type, providing a cascade-type structure for an improved electron flow (higher FF). The polysulfide solution enters in an intimate contact with the photoanode surface to renew the transferred electrons from Mn-CdS and ensures the stability of sensitizers.

Conversely, an energetic barrier is provided in the CdS/Bi<sub>2</sub>S<sub>3</sub> heterostructure via CB, where the electrons in CdS are injected to Bi<sub>2</sub>S<sub>3</sub>, decreasing the electron lifetime and the generated photocurrent by the photovoltaic device. The corresponding PCE values of champion devices before and after Mn-modification into the composites were estimated to be 1.01 % and 1.63 %, respectively. These values are higher than those in conventional Bi<sub>2</sub>S<sub>3</sub>-based solar cells,<sup>58-61,113</sup> which means an improvement of photovoltaic performance of these kind of devices by using the studied photoanodes.

**Table 7.** Solar cell parameters estimated for ZnS layer-covered BNF-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> and BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite photoanodes at 1 sun.

Photoanode	J <sub>sc</sub> / mAcm <sup>-2</sup>	V <sub>oc</sub> / V	FF	PCE / %
4-CdS-2-Bi <sub>2</sub> S <sub>3</sub>	2.86 ± 0.15	$0.67 \pm 0.02$	$0.44 \pm 0.05$	$0.84 \pm 0.14$
Champion*	2.99	0.69	0.49	1.01
0.7-Mn-4-CdS-2-Bi <sub>2</sub> S <sub>3</sub>	3.91 ± 0.34	$0.74 \pm 0.02$	0.52 ± 0.11	1.50 ± 0.18
Champion*	3.96	0.72	0.57	1.63

\*QDSSC device with the highest photoconversion efficiency obtained from three samples.

To validate the generation of a viable pathway for electron mobility from  $Bi_2S_3$  to back contact, mediated by  $Mn^{2+}$  into CdS, band structure of Mn-composite was determined, achieving the associated energy of VB and CB edge ( $E_{VB}$  and  $E_{CB}$ , respectively) into the Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> heterojunction. By using the extrapolation method in normalized XPS VB spectra of BNF-TNTs, Mn-CdS and Bi<sub>2</sub>S<sub>3</sub> (Appx. M), their corresponding  $E_{VB}$  were estimated to be 1.84, 0.71 and -0.13 eV, respectively. Then,  $E_{CB}$  was calculated by the following equation (15):

$$E_{CB} = E_{VB} - E_g \tag{15}$$

As seen in Fig. 27, low driving force in the CdS/Bi<sub>2</sub>S<sub>3</sub> heterojunction blocks charge carrier separation and transfer to BNF-TNTs, which is the main reason of a lower energy conversion and higher electron recombination rate into a QDSSC. Nonetheless, Mn<sup>2+</sup> states below CB edge of CdS increase driving force for a more efficient electron flow to back contact, and thereby a higher PCE is achieved.

**Figure 27.** Influence of  $Mn^{2+}$  on the electron transport ability of BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite.



Accordingly, a charge carrier transport mechanism was proposed to explain the enhancement in the PCE of device by the presence of  $Mn^{2+}$ . Outer Bi<sub>2</sub>S<sub>3</sub> can harvest high low-energy photons from sunlight, generating electron-hole pairs. Through the cascade type-heterojunction provided by a lowered CB from Mn-CdS, electrons can be injected from Bi<sub>2</sub>S<sub>3</sub> to Mn<sup>2+</sup> levels and then transferred to BNF-TNTs, increasing the V<sub>oc</sub> of the cell. Ti<sup>3+</sup> donor states in the latter semiconductor can also inject electrons to Cd-Cd energy levels into Mn-CdS which are excited toward Mn<sup>2+</sup> levels requiring an energy around 2.16 eV. Simultaneously, photogenerated electrons into Bi<sub>2</sub>S<sub>3</sub> can be excited to Mn<sup>2+</sup> promoting an indirect transition. Here, the electron recombination is inhibited in the BNF-TNTs/Mn-CdS/Bi<sub>2</sub>S<sub>3</sub>/electrolyte interface, flowing more electrons to the back contact to obtain a high J<sub>sc</sub> and FF. Finally, the electrons are transported to the Cu<sub>2</sub>S/cu cathode to renew the S<sup>2-</sup>/Sn<sup>2-</sup> redox couple.

Lastly, by observing the PCE of champion solar devices achieved through their corresponding J-V characteristics, (Section 4.1, 4.2 and 4.3) the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> co-sensitized photoanodes are suitable to develop a high phovoltaic performance in a conventional QDSSC. Compared with a single sensitization (in the case of CdSesensitized materials) both CdS and CdS<sub>1-x</sub>Se<sub>x</sub> improve the light harvesting in a wide spectral region, generating more carriers to be transported into the device. On the other hand, although the photoanode composed by Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> heterojunction also induce the formation of a high number of carriers under illumination, a low driving force can be achieved in the Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interface, which hinder the electron flow into the cell (it is related to the low J<sub>sc</sub>). Even so, the Mn incorporation affect positively the carrier transport into the composite. By modulating the Se content into the CdS<sub>1-x</sub>Se<sub>x</sub>, a balance between adequate band alignment and lowenergy harvesting ability into the photoanode can be reached, facilitating that a high number of carriers can be transported to the current collector. Hence, according with Table 8, the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> based solar cell generated a higher PCE around 137 % and 158 % than those BNF-5-CdSe and 0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> ones, respectively.

**Table 8.** Comparison of photoconversion efficiencies in the champion solar devices

 achieved to use different composite photoanodes.

Photoanode	PCE / %
BNF-5-CdSe	1.88
BNF-4-CdS-5-CdS <sub>1-x</sub> Se <sub>x</sub>	2.58
0.7-Mn-4-CdS-2-Bi <sub>2</sub> S <sub>3</sub>	1.63

In this section, it can be concluded that the Mn-modification of Cd-chalcogenides based sensitizers provided the improvement of both the light harvesting and electron transportation ability into BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites. By changing the amount of incorporated Mn<sup>2+</sup> into CdS, the optical and semiconducting properties of
composites were modified, altering the band structure of the BNF-TNTs/Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> heterojunction. Here, the formation of a suitable band alignment into composite was promoted by using a Mn content around X = 0.7 at.%, achieving an efficient charge carrier mobility from the Bi<sub>2</sub>S<sub>3</sub>/electrolyte interface to BNF-TNTs. The carrier recombination was hindered, which increased PEC performance, electron lifetime and decreased electron recombination rate into the material.

On the other hand, by exceeding the Mn<sup>2+</sup> content over 0.7 at.%, a I-type heterostructure was formed due to the mismatch of conduction band edges in the BNF-TNTs/Mn-CdS interface. The charge carrier separation was blocked, causing a low electron flow reaching the back contact. According with the latter, the photoelectrochemistry can predict the photovoltaic performance of a photoanode in a sensitized solar device by studying the PEC properties of photoanodes during band engineering. In this way, the photoconversion efficiency of mismatched binary chalcogenide based QDSSCs can be enhanced. the PCE of a QDSSC using the BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> photoanode was around 1.63 %, under 1 sun conditions. This value is higher than that of PCE of conventional Bi<sub>2</sub>S<sub>3</sub>-based solar cells. Current efforts should also be addressed to the fabrication of Mn chalcogenide-sensitized solid-state solar cells, to separate charge carrier more efficiently into the composites and avoid loss of PCE by recombination.

### 5. CONCLUSIONS

- The PCE of QDSSCs by using a cadmium chalcogenide QDs-sensitized BNF-TNTs as photoanode, depends mainly on the light harvesting and charge carrier transport capability into composite, which is enhanced after B-doping. In this sense, a suitable amount of boron and chalcogenide QDs load promotes an efficient electron flow in the BNF-TNTs/chalcogenide interface, increasing the photovoltaic performance of solar device. The synergistic behaviour between B-doping and chalcogenide sensitization allowed to achieve a maximum PCE around 2.58 %, which is higher than some performances reported for conventional QDSSCs.
- The origin of synergism in CdSe-sensitized BNF-TNTs based photoanodes occurs by direct charge carrier transport from Ti<sup>3+</sup> energy levels into TiO<sub>2</sub>, to valence band of chalcogenide, in the BNF-TNTs/CdSe interface. The effectiveness of this process depends on the suitable amount of formed Ti<sup>3+</sup> which is related with the adequate amount of boron precursor to carry out the B-doping. In this way, the photo(electro)chemical and photovoltaic properties of BNF-Y-CdSe modified materials are enhanced.
- The SILAR method allows to prepare CdS QDs forming Cd-Cd energy levels located above the valence band. These "silent" energy levels produce changes in the optical and electronic properties into the chalcogenide, maximizing/lowering the light harvesting, charge carrier transport abilities and PCE into a BNF-Y-CdS composite photoanode. On the other hand, the deposition of an outer sensitizer as CdS<sub>1-x</sub>Se<sub>x</sub> on BNF-Y-CdS increases the PCE performance of a device as result of a good balance between low-energy absorption and suitable band alignment into composite. However, the potentiality of the photoanode as light-harvester is limited by the "silent" levels acting as recombination centers for electrons flowing into the device.

The Mn-doping of CdS used as a "bridge" sensitizer generates a suitable pathway for the electron transport, to make suitable the poor band alignment in the BNF-TNTs/CdS/Bi<sub>2</sub>S<sub>3</sub> interface, and thereby improve the phovoltaic performance of a device. Mn<sup>2+</sup> states lower the band gap of CdS, which enhances low-energy harvesting of BNF-X-Mn-Y-CdS-2-Bi<sub>2</sub>S<sub>3</sub> photoanodes, decreases carrier recombination rate, and increases electron transport to the back contact. These changes can be followed through of study of their photo(electro)chemical properties to predict if a photoanode is useful for a photovoltaic process.

### 6. **RECOMMENDATIONS**

- Efforts should be focused in studying combinations of metal or/and other non-metal doped-TNTs with chalcogenides, to take advantage from synergistic behaviour of doping and sensitization to enhance the PCE of QDSSCs.
- It is recommended to deepen about the decrease of Cd-Cd bondings using other kind of preparation methods of composites, for instance, chemical bath deposition or organic linking, because of these "silent" energy levels (not discussed in reported works about photovoltaics before) impacts the overall PCE value of cell.
- Current efforts should also be addressed to the fabrication of Mn-chalcogenide-sensitized solid-state solar cells, to separate charge carrier more efficiently into the composites and avoid loss of PCE by recombination.
- Hot topic materials as perovskite nanocrystals could be combined with chalcogenide-based materials to improve the photovoltaic performance of QDSSCs.

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#### APPENDIX

# Appendix A. Characterization of light source used during photoelectrochemical measurements

**Fig. A1.** Emission spectrum of the halide lamp used in photo(electro)chemical tests (60 mW cm<sup>-2</sup>).



# Appendix B. Dependence of depletion layer (W) on the boron doping in the photoanodes

One alternative to observe changes in the charge carrier density by impurity doping, is through the estimation of depletion layer width (W) produced during band bending of TiO<sub>2</sub> (See Fig. B1a). W can be determined by the following relationship considering the terms used in the M-S analysis (12):

$$W = \sqrt{\frac{2\varepsilon\varepsilon_0(E_{app} - E_{fb})}{eN_d}} \tag{12}$$

Here, e is the electron charge. W was plotted vs E<sub>app</sub>-E<sub>fb</sub> for all photoanodes, obtaining a decrease of depletion layer for  $E_{app}-E_{fb} = 1.0 V_{Ag/AgCl}$  to vary the amount of  $H_3BO_3$  in the following order: 0.09 wt% < 0.06 wt% < 0.04 wt% < bare NF-TNTs. Some works have reported that a wide W is vital for an efficient charge carrier separation to increase the photoresponse of TiO<sub>2</sub>.<sup>86,87</sup> Nonetheless, X-BNF-TNTs showed a diminution of W (See Fig. B1b). So, ¿what allows the PEC performance of modified photoanodes increases although W is decreased by boron doping? The answer was addressed in terms of the donor species function into X-BNF-TNTs formed by interstitial boron. After boron doping, the amount of Ti<sup>3+</sup> species was increased than that bare NF-TNTs, mediating a suitable electron-hole separation by using a H<sub>3</sub>BO<sub>3</sub> content of 0.06 wt%. It is suggested that a high amount of Ti<sup>3+</sup> was formed in the bulk and the depletion layer of B-photoanodes (N<sub>d</sub> of 0.06-BNF-TNTs was 3.6 times higher than that NF-TNTs). This modification facilitated electron-hole pair separation to generate a high photocurrent.<sup>29,44</sup> Conversely, an excess of Ti<sup>3+</sup> in the bulk and W of TNTs favoured charge-carrier recombination, which inhibited photoholes migration to the photoanode surface and electron transport to the current collector. On the other hand, E<sub>fb</sub> can be considered as indication of the energy required to carry out charge carrier separation. Thus, the flat band condition (absence of W) into TNTs could be easily achieved at more negative values to increase the amount of H<sub>3</sub>BO<sub>3</sub>.

**Fig. B1.** a) Depletion layer (W) as a function of applied potential for the NF-TNTs and X-BNF-TNTs photoanodes, and b) schematic representation of W compaction varying the amount of H<sub>3</sub>BO<sub>3</sub>.



Appendix C. Wettability of CdSe-sensitized photoanodes

Contact angle (CA) measurements were carried out for 0.06-BNF-TNTs photoanodes before (Fig. C1a) and after 5-CdSe sensitization (Fig. C1b), dropping 10 µL of DI water on the photoanode at room temperature. Bare BNF-TNTs presented a high CA about 93.1°, which indicates a low wettability in its surface. The high surface tension of water provides a poor wetting ability on the solid surface, hindering the penetration of the liquid into the BNF-TNTs matrix. In addition, after annealing, the hydroxyl groups in the TNTs surface are replaced by oxygen molecules, which decrease their hydrophilicity.<sup>114</sup> This evidence have been considered to avoid the use of SILAR aqueous solutions to carry out sensitization processes.<sup>69</sup> Conversely, after 5-CdSe sensitization, the CA was decreased until 53.0°, indication of the improvement in the hydrophilicity of composite material. The chalcogenides deposition generates a more roughness surface,<sup>69</sup> facilitating the permeability of liquid. It favours an intimate contact between the composite and the

electrolyte to promote the diffusion of redox species and the charge carrier transport in the photoanode/electrolyte interface.<sup>114</sup>

**Fig. C1.** Contact angle measurements for 0.06-BNF-TNTs a) before and b) after 5-CdSe sensitization.



# Appendix D. Influence of boron modification and CdSe sensitization on the conducting properties of composites

As mentioned above, electrochemical impedance spectroscopy (EIS) spectra were acquired to investigate the interfacial charge carrier transfer behaviour into BNF-Y-CdSe materials. Under dark, typical Nyquist plots for each composite in function of number of SILAR cycles (Fig. D1a) were fitted to a serie resistance (R<sub>s</sub>) and two-Randles type circuits in serie, which indicate the existence of two interfaces into the 0.06-BNF-Y-CdSe. From the impedance parameters depicted in Table D1, R<sub>s</sub> was associated to the ITO resistance and the electrical contact from the external circuit of cell. R<sub>1</sub> and CPE<sub>1</sub> corresponded to the resistance and constant phase element of the ITO/BNF-TNTs/Y-CdSe interface (inset of Fig. D1a), while the interfacial charge carrier resistance (R<sub>ct</sub>) and capacitance (CPE<sub>2</sub>) were associated to the BNF-Y-CdSe/electrolyte interface.<sup>29,64</sup> It could be noted from Table D1, that R<sub>1</sub> showed a decrease-to-increase behaviour with the increase of SILAR cycles until 5.

The declining of R<sub>1</sub> indicates the enhancement of charge carrier transfer from CdSe to BNF-TNTs assisted by the type-II heterojunction in the BNF-TNTs/CdSe interface. Moreover, the R<sub>ct</sub> also displayed a notable decrease to sensitize the BNF-TNTs with 5-CdSe, which means an effective photogenerated electron hole pairs separation inside CdSe mediated by Ti<sup>3+</sup> donor states, and the inhibition of electron recombination with the S<sup>2-</sup> based electrolyte. <sup>39,115</sup> In addition, the accumulation of electrons in the heterostructure was promoted, leading to the highest CPE2. Conversely, upon 6-CdSe sensitization, R<sub>1</sub> and R<sub>ct</sub> were increased, as result of a low electron recombination resistance the into heterostructure, and the photoanode/electrolyte interface. It facilitates fast electron recombination in CdSe with the electrolyte. This was corroborated to obtain a lower CPE<sub>2</sub> than 5-CdSe.

**Fig. D1.** Electrochemical impedance spectroscopy (EIS) spectra (10 kHz-0.01Hz) for a) BNF-Y-CdSe photoanodes under dark. b) EIS spectra of NF-5-CdSe and BNF-5-CdSe composites under visible light. c) the equivalent circuit after EIS spectra. Electrolyte: 1.0 M Na<sub>2</sub>S (pH 12). Insets of Fig. D1a,b show the Nyquist plots at high frequencies for the composites.



On the other hand, the effect of B-doping on the improvement of photogenerated charge carrier transport into the BNF-5-CdSe was also observed in EIS spectra performed under visible illumination (Fig.D1b). By comparing with a NF-5-CdSe photoanode, a decrease in R<sub>I</sub> (inset of Fig. D1b) and R<sub>ct</sub> were observed. A high Ti<sup>3+</sup> content promoted by B-doping increases the charge carriers separated and transported from the B-composite photoanode/electrolyte interface to the back contact. The increase of carriers transferred from BNF-TNTs to CdSe into BNF-5-CdSe was corroborated by a higher CPE<sub>2</sub> than that NF-5-CdSe composite.

**Table D1.** Parameters determined from EIS fitting of NF-5-CdSe and BNF-Y-CdSe composites

Photoanode	Rs / Ωcm <sup>-2</sup>	R <sub>I</sub> / Ωcm <sup>-2</sup>	R <sub>ct</sub> / Ωcm <sup>-2</sup>	CPE <sub>1</sub> /	CPE <sub>2</sub> /
				µFcm <sup>-2</sup>	µFcm <sup>-2</sup>
3-CdSe, dark	68	697	7742	67	238
4-CdSe, dark	63	675	7205	53	954
5-CdSe, dark	66	145	6583	11	1267
6-CdSe, dark	67	344	11423	34	692
NF-5-CdSe, light	137	92	660	348	2344
BNF-5-CdSe, light	150	23	403	106	3803

### Appendix E. Distribution of elements and co-existence of Cd-chalcogenides on BNF-TNTs

Fig. E1 depicts the STEM-mapping of the BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composite to observe the distribution of the elements in the material (Fig. E1a). Ti and O atoms were located along of the tubular structure, while F, Cd, S and Se were found to be on the nanotube surface in a minor load. According with the identification, the amount of S was much higher than that Se. This was due to sulfur atoms did not

only derive from the CdS<sub>1-x</sub>Se<sub>x</sub> alloy, but also from the inner CdS deposited previously on the BNF-TNTs.

**Fig. E1.** a) STEM-mapping of the BNF-4-CdS-5-CdS<sub>0.50</sub>Se<sub>0.50</sub> photoanodes. b) Raman spectra of the BNF-TNTs before and after 4-CdS and 5-CdS<sub>0.50</sub>Se<sub>0.50</sub> sensitizations. The anatase (A) phase is shown as Raman peaks. Inset of Fig. 2b shows the deconvolution of CdS and CdS<sub>0.50</sub>Se<sub>0.50</sub> peaks into the Raman spectrum of BNF-4-CdS-5-CdS<sub>0.50</sub>Se<sub>0.50</sub> photoanode.



On the other hand, micro-Raman scattering analysis were conducted to the BNF-TNTs, BNF-4-CdS and BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> composites to corroborate the composition presented in each material (Fig. E1b). Bare BNF-TNTs showed 4 peaks at (142.3, 191.2, 393.6, and 635.5) cm<sup>-1</sup> attributed to the anatase phase of TiO<sub>2</sub>. After 4-CdS sensitization, the most intense peak at 142.3 cm<sup>-1</sup> disappeared and two new peaks appeared at 293.2 cm<sup>-1</sup> and 589.7 cm<sup>-1</sup>. These peaks were ascribed to the longitudinal optical (LO) phonon frequencies of CdS.<sup>73,116</sup> After 5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitization, two representative peaks were achieved at (200, 293.2, 395, 472.3, 486.5 and 582.3) cm<sup>-1</sup>. The presence of the latter signals was associated to the

combination of LO phonons of CdS and CdSe in the CdS<sub>1-x</sub>Se<sub>x</sub>.<sup>73</sup> These results corroborate the formation of 4-CdS and 5-CdS<sub>1-x</sub>Se<sub>x</sub> after BNF-TNTs SILAR sensitization.

### Appendix F. Chemical environment of BNF-TNTs

**Fig. F1.** High-resolution XPS a) N 1s, b) F 1s, c) B 1s and d) Ti 2p of the BNF-TNTs based photoanodes.



## Appendix. G. Stability of CuS/FTO and Cu<sub>2</sub>S/Cu based cathodes used in 4-CdS-QDSSCs

**Fig. G1.** Photographs of a) CuS/FTO and b) Cu<sub>2</sub>S/Cu based cathodes before and after photovoltaic measurements.



## Appendix H. Electrochemical Impedance spectra of Y-CdS- and CdS<sub>1-x</sub>Se<sub>x</sub>-sensitized BNF-TNTs

The carrier transport capability of the BNF-Y-CdS varying the load of CdS QDs deposited by SILAR method was studied by EIS under visible illumination (Fig. H1). To understand the interfacial process occurring in the composites, Nyquist plots obtained for each material were fitted with a serie resistance and two Randles-type circuits connected in serie. This rearrangement was associated to the presence of

two interfaces into BNF-Y-CdS composites. EIS parameters obtained from the fitted plots are shown in Table H1.  $R_s$  was the ITO resistance/contact from the external circuit of cell.  $R_1$  and CPE<sub>1</sub> were ascribed to electron transport ability and capacitance in the ITO/BNF-TNTs/CdS interfaces, while  $R_2$  and CPE<sub>2</sub> were associated to interfacial carrier transfer resistance and its corresponding capacitance in the BNF-Y-CdS/electrolyte interfaces.<sup>90,92,96</sup>

It was noteworthy from Table H1 that R1 and R2 were diminished to increase the SILAR cycles until 4. The decrease of the resistance values in each interface is the evidence of facilitated carrier transport from the electrolyte to CdS QDs, which can oxidize the S<sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> redox couple in the photoanode/electrolyte interface and avoid its photodecomposition. The accumulation of the sulfur species on the BNF-4-CdS surface could be observed to obtain a higher CPE2 than those the others photoanodes. It agrees with the increase of signals of adsorbed species seen in photopotential measurements. Then, accumulated photoelectrons in the CdS are injected via CB to BNF-TNTs, mediated by a suitable II-type heterojunction.<sup>36,48</sup> The enhancement of the conducting properties of composite was noted to evidence the lowest CPE<sub>1</sub>, associated to an efficient charge carrier separation into the BNF-4-CdS photoanode. Conversely, after 5-CdSe and 6-CdSe sensitization, R1 and R2 values were increased while the CPE<sub>1</sub> and CPE<sub>2</sub> showed an increase/decrease behaviour. The charge carrier accumulation in the BNF-5-CdS and BNF-6-CdS interface is the main indication of electron injection suppressing into CB of BNF-TNTs from CdS QDs, where a high likelihood of charge carrier recombination can be achieved. Although the incorporation of Cd-Cd energy states increases the ability of CdS to capture lower-energy photons decreasing its E<sub>g</sub> without shifting the CB edge,<sup>52</sup> an excess of Cd-Cd energy levels can act as recombination centers, blocking electron transfer in the composite.

**Fig. H1.** Nyquist plots (10 kHz – 0.01 Hz) of BNF-Y-CdS photoanodes in function of number of SILAR cycles (Y). Insets of Fig. H1 show the Nyquist semicircle at high frequencies and equivalent circuit after EIS spectra fitting. Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination source: halide lamp (60 mWcm<sup>-2</sup>).



**Table H1.** Fitted EIS parameters of BNF-Y-CdS photoanodes.

Photoanode	Rs / Ωcm <sup>-2</sup>	R <sub>I</sub> / Ωcm <sup>-2</sup>	R <sub>ct</sub> / Ωcm <sup>-2</sup>	CPE <sub>1</sub> /	CPE <sub>2</sub> /
				µFcm <sup>-2</sup>	µFcm <sup>-2</sup>
Bare BNF-TNTs	25	930	51485	36	49
3-CdS	48	342	2154	49	69
4-CdS	60	93	938	12	2310
5-CdS	57	220	1392	16	562
6-CdS	67	277	2487	35	792

The 5-CdS<sub>1-x</sub>Se<sub>x</sub> sensitization of BNF-4-CdS also caused changes in the conducting properties of the composites, which were studied by electrochemical impedance spectroscopy (EIS) through Nyquist plots (Fig. H2). Similar for the BNF-Y-CdS

described above, two semicircles were obtained in the corresponding EIS spectra and fitted to a two Randles-type circuits connected in serie. R<sub>s</sub> was associated to the connection between conducting glass substrate and the external circuit of the cell. R<sub>1</sub> and CPE<sub>1</sub> were ascribed to carrier transfer and accumulation processes in the BNF-TNTs/CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interfaces, while R<sub>2</sub> and CPE<sub>2</sub> corresponded to electron transport ability in the CdS/CdS<sub>1-x</sub>Se<sub>x</sub>/electrolyte interface.<sup>36,48</sup> EIS parameters extracted from the respective Nyquist curves are displayed in Table H2, where showed a widely dependence on the S/Se molar ratio in the alloy. To decrease the S/Se to 1.0, R<sub>1</sub>, R<sub>2</sub> and CPE<sub>1</sub> were also decreased, indication of an efficient electronhole pair separation into the CdS<sub>1-x</sub>Se<sub>x</sub>, and electron transport from this sensitizer to BNF-TNTs using the CdS as a "charge bridge". The II-type heterojunction in the CdS/CdS<sub>1-x</sub>Se<sub>x</sub> interface promoted electron injection to CdS via CB, avoiding the charge recombination.<sup>26</sup>

A low electron mobility resistance increases the charge carrier lifetime in the composite, agreeing with a slow OCPD observed in photopotential measurements. More electrolyte species can renew the electrons in the CdS<sub>1-x</sub>Se<sub>x</sub>, increasing the CPE<sub>2</sub> value. For S/Se < 0.5, R<sub>1</sub>, R<sub>2</sub> and CPE<sub>1</sub> were increased, while the CPE<sub>2</sub> value was decreased. Here, the electron accumulation mediated by I-type heterojunction promotes carrier recombination in the co-sensitizers interface. Thus, a low amount of sulfur species is accumulated in the CdS<sub>1-x</sub>Se<sub>x</sub>/electrolyte interface to inject electrons to the ternary alloy. Despite the unsuitable band alignment in the CdS/CdSe interface observed by the highest R<sub>1</sub> and CPE<sub>1</sub>, the corresponding R<sub>2</sub> and CPE<sub>2</sub> values were lower than that composite with S/Se = 0.5. This suggested that CdSe could photogenerate charge carriers which were separated and injected to a Cd-Cd energy states into CdS, renewing the electrons in CdSe by the electrolyte. However, the electrons promoted to the CB of CdS could returned to CdSe via CB, mediating electron recombination with oxidized sulfur species from S<sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> redox couple.<sup>32,48</sup>

**Fig. H2.** Nyquist plots (20 kHz–0.01 Hz) of BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> photoanodes in function of S/Se molar ratio into ternary alloy. Insets of Fig. H2 show the Nyquist semicircle at high frequencies and equivalent circuit after EIS spectra fitting. Electrolyte: 0.25 M Na<sub>2</sub>S + 0.35 M Na<sub>2</sub>SO<sub>3</sub> (pH 12), illumination source: halide lamp (60 mWcm<sup>-2</sup>).



 Table H2.
 Fitted EIS parameters of BNF-4-CdS-5-CdS1-xSex photoanodes.

Photoanode	Rs / Ωcm <sup>-2</sup>	R <sub>I</sub> / Ωcm <sup>-2</sup>	R <sub>ct</sub> / Ωcm <sup>-2</sup>	CPE1/	CPE <sub>2</sub> /
				µFcm <sup>-2</sup>	µFcm <sup>-2</sup>
5-CdS <sub>0.67</sub> Se <sub>0.33</sub>	51	59	1315	111	2008
5-CdS <sub>0.50</sub> Se <sub>0.50</sub>	64	31	575	40	3377
5-CdS <sub>0.33</sub> Se <sub>0.67</sub>	58	38	2771	47	1710
5-CdSe	94	132	2344	68	1042

# Appendix I. Valence band edge (EVB) determination in BNF-4-CdS-5-CdS1-xSex composites

By extrapolating to 0 eV the corresponding slopes in the XPS valence band spectra for the studied materials, the E<sub>VB</sub> values were estimated to be (2.14, 0.84, 0.46, 0.44, 0.41, and 0.32) eV for BNF-TNTs, BNF-4-CdS, BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> (S/Se = 2.0, 1.0, 0.5 and 0, respectively) (Fig. 11). Their conduction band edges (E<sub>CB</sub>) were calculated by using the equation (8), and converted to potential scale vs Ag/AgCl, 3 M KCl (+210 mV vs NHE) by equation (14) above. Both the E<sub>CB</sub> and E<sub>VB</sub> were narrowed to increase the amount of added Se into ternary alloy, establishing a balance between light harvesting and band alignment in the formed CdS/CdS<sub>1-x</sub>Se<sub>x</sub> heterostructure.

**Fig. 11.** Normalized XPS valence band spectra of BNF-TNTs, BNF-4-CdS and BNF-4-CdS-5-CdS<sub>1-x</sub>Se<sub>x</sub> photoanodes varying the Se content into ternary alloy.



### Appendix J. Cd-Cd energy levels into CdS sensitized BNF-TNTs

**Fig. J1.** Schematic representation Cd-Cd energy states formation during CdS deposition on BNF-TNTs surface.



Appendix K. Chemical environment of BNF-TNTs grown on Ti

Fig. K1 shows the chemical environment of a BNF-TNTs directly analyzed by XPS on Ti substrate. The chemical species of boron, nitrogen and fluorine confirm the B, N, F- tridoping of TiO<sub>2</sub> nanotubes after Ti anodization. On the other hand, Fig. K2 depicts the high-resolution XPS S 2p for the BNF-0.7-Mn-4-CdS composite. The presence of doublets at low binding energies (BEs) is ascribed to the presence of CdS in the material, and the signals at high BEs is associated to the partial oxidation of the chalcogenide surface.<sup>107</sup>
**Fig. K1.** High-resolution XPS a) N 1s, b) F 1s, c) B 1s and d) Ti 2p spectra of BNF-TNTs on Ti.



Fig. K2. High-resolution XPS S 2p spectrum of BNF-0.7-Mn-4-CdS composite.



# Appendix. L. Electrochemical impedance spectra of BNF-X-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites

The conducting properties of composites with and without Mn modification were studied by electrochemical impedance spectroscopy (EIS) as response of their corresponding charge carrier transportation capability (Fig. L1). Nyquist plots were obtained under visible light and fitted with equivalent circuits associated to two Randles-type models connected in serie. This approach indicates the co-existence of two interfaces into the photoanodes. From EIS parameters summarized in Table L1, Rs was ascribed to the unavoidable resistance existing in the external contact of cell. R1 **CPE**<sub>1</sub> the and denoted the carrier mobility into the BNF-TNTs/Cd-sensitizer/Bi<sub>2</sub>S<sub>3</sub> interface, while R<sub>2</sub> and CPE<sub>2</sub> represented the interfacial charge carrier transfer in the Cd-sensitizer/Bi<sub>2</sub>S<sub>3</sub>/electrolyte interface.<sup>90</sup>

As seen in Table L1, low R<sub>1</sub> and R<sub>2</sub> in the BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composite is an indication of an efficient electron transport from outer Bi<sub>2</sub>S<sub>3</sub>/electrolyte interface to BNF-TNTs mediated by Mn-modified CdS. An adequate band heterostructure is achieved by incorporation of Mn<sup>2+</sup> states close to CdS CB.<sup>63,67</sup> In consequence, more photoholes can be accumulated in the Mn-composite to react with S<sup>2</sup>/SO<sub>3</sub><sup>2-</sup> redox couple. Thus, higher CPE<sub>2</sub> was obtained than that BNF-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub>. Conversely, EIS parameters corroborated that the latter material exhibited a poor band alignment for a direct electron injection in the CdS/Bi<sub>2</sub>S<sub>3</sub> via CB. High electron transport resistance into CdS/Bi<sub>2</sub>S<sub>3</sub> interface decreases the number of available holes in the photoanode and thereby a low S<sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> species content can be accumulated in the photoanode surface (low CPE<sub>2</sub>). Returned electrons to outer sensitizer can also be recombined with the sacrificial agent, increasing the likelihood of eventual photodecomposition. **Fig. L1.** Nyquist plots (100 kHz–0.01 Hz) of BNF-TNTs/Cd-sensitizer/Bi<sub>2</sub>S<sub>3</sub> composites. Insets of Fig. L1 show the Nyquist semicircle at high frequencies and equivalent circuit after EIS spectra fitting. Electrolyte:  $0.25 \text{ M} \text{ Na}_2\text{S} + 0.35 \text{ M} \text{ Na}_2\text{SO}_3$  (pH 12), illumination source: halide lamp (60 mWcm<sup>-2</sup>).



Table L1. Fitted EIS parameters of BNF-TNTs/Cd-sensitizer/Bi<sub>2</sub>S<sub>3</sub> composites

Photoanode	Rs / Ωcm <sup>-2</sup>	Rı / Ωcm <sup>-2</sup>	R <sub>ct</sub> / Ωcm <sup>-2</sup>	CPE <sub>1</sub> /	CPE <sub>2</sub> /
				µFcm <sup>-2</sup>	µFcm <sup>-2</sup>
4-CdS-2-Bi <sub>2</sub> S <sub>3</sub>	2	12	454	14434	7768
0.7-Mn-4-CdS-2-Bi <sub>2</sub> S <sub>3</sub>	4	2	296	9046	9114

## Appendix M. Valence band edge determination in BNF-TNTs/Mn-CdS/Bi<sub>2</sub>S<sub>3</sub> interface

**Fig. M1.** Normalized XPS valence band spectra of BNF-TNTs, BNF-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> and BNF-0.7-Mn-4-CdS-2-Bi<sub>2</sub>S<sub>3</sub> composites.



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### Appendix N. Participation in national and international events

- **N1.** National events:
- <u>A. F. Gualdron-Reyes</u>, A. M. Meléndez, M. E. Niño-Gómez. I Congreso Colombiano de Electroquímica, Zipaquirá, Colombia, 2014. Poster presentation: El papel de las propiedades semiconductoras de electrodos B-TiO<sub>2</sub> grafeno/acero inoxidable en la oxidación de fenol (first-prize winner).
- <u>A. F. Gualdron-Reyes</u>, A. M. Meléndez, M. E. Niño-Gómez. II Congreso Colombiano de Electroquímica, Bucaramanga, Colombia, 2016. Poster presentation: Mejoramiento del rendimiento fotoelectroquímico de fotoánodos transparentes basados en nanotubos de B-TiO<sub>2</sub>/ITO bajo luz visible.
- **N2.** International events:
- <u>A. F. Gualdron-Reyes</u>, A. M. Meléndez, M. E. Niño-Gómez. XXIII International Materials Research Congress 2014, Cancún, México, 2014. Poster presentation: Effect of the substrate on the photoelectrochemical activity of boron doped TiO<sub>2</sub>/graphene composite films in phenol oxidation.
- F. J. Mancilla, S. F. Rojas, <u>A. F. Gualdrón-Reyes</u>, M. E. Niño-Gómez. XXII Congreso de la Sociedad Iberoamericana de Electroquímica-SIBAE, San José, Costa Rica, 2016. Poster presentation: Preparación de fotoánodos basados en B-TiO<sub>2</sub>/Ti activos a la luz visible para la oxidación fotoelectroquímica de glicerol.
- 5. **4th Latin American Congress of Photocatalysis, Photoelectrochemical and Photobiology**, Piedecuesta, Colombia, 2016. Poster presentations:

- D. F. Rivera, L. J. Hoyos, <u>A. F. Gualdrón-Reyes</u>, M. E. Niño-Gómez Fabrication of Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanotubes array electrodes for enhanced photoelectrocatalytic glycerol oxidation (first-prize winner).
- A. L. Cárdenas, <u>A. F. Gualdrón-Reyes</u>, A. M. Meléndez. Fabrication of oriented TiO<sub>2</sub> Nanotubes Membranes on ITO glass as photoanodes for solar cells (first-prize winner).
- J. S. Ríos, <u>A. F. Gualdrón-Reyes</u>, M. E. Niño-Gómez. 21<sup>st</sup> Topic Meeting of the International Society of Electrochemistry, Szeged, Hungary, 2017. Oral presentation: Influence of Cd/Mn ratio on the photoelectrochemical properties of Cd<sub>1-x</sub>Mn<sub>x</sub>S/Bi<sub>2</sub>S<sub>3</sub> co-sensitized boron-doped TiO<sub>2</sub> nanotubes.

#### **Appendix O. Publications**

- F. J. Mancilla, S. F. Rojas, <u>A. F. Gualdrón-Reyes</u>, M. I. Carreño-Lizcano, L. J. Duarte, M. E. Niño-Gómez, Improving the photoelectrocatalytic performance of boron modified TiO<sub>2</sub>/Ti sol-gel based electrodes for glycerol oxidation under visible illumination. *RSC Advances*, 2016, 6, 46668.
- <u>A. F. Gualdrón-Reyes</u>, A. Cárdenas-Arenas, C. A. Martínez, V. V. Kouznetsov, A. M. Meléndez. Fabrication of transparent TiO<sub>2</sub> nanotube-based photoanodes for CdS/CdTe quantum co-sensitized solar cells. *Journal of Physics: Conference Series*, 2017, 786, 012044.
- A. F. Gualdrón-Reyes, V. Domínguez-Vélez, J. A. Morales-Morales, R. Cabanzo, A. M. Meléndez. Effect of substrate nature on the electrochemical deposition of calcium-deficient hydroxyapatites. *Journal of Physics: Conference Series*, 2017, 786, 012030.
- L. J. Hoyos, D. F. Rivera, <u>A. F. Gualdrón-Reyes</u>, R. Ospina, J. Rodríguez-Pereira, J. L. Ropero-Vega, M. E. Niño-Gómez. Influence of immersion cycles during n-β-Bi<sub>2</sub>O<sub>3</sub> sensitization on the photoelectrochemical behaviour of N-Fcodoped TiO<sub>2</sub> nanotubes. *Applied Surface Science*, 2017, 423, 917.
- A. F. Gualdrón-Reyes, A. M. Meléndez, I. González, L. Lartundo-Rojas, M. E. Niño-Gómez. Effect of metal substrate on photoelectrocatalytic activity of B-doped graphene modified TiO<sub>2</sub> thin films: role of iron oxide nanoparticles at grain boundaries of TiO<sub>2</sub>. *Journal of Physical Chemistry C*, 2018, 122, 297.

- <u>A. F. Gualdrón-Reyes</u>, A. M. Meléndez, M. A. Mejía Escobar, F. Jaramillo, M. E. Niño-Gómez. The role of boron in the carrier transport improvement of CdSe-sensitized B,N,F-TiO<sub>2</sub> nanotubes solar cells: a synergistic strategy. *New Journal of Chemistry*, 2018, 42, 14481.
- A. F. Gualdrón-Reyes, Y. S. Joon, I. Mora-Seró, Recent insights for achieving mixed halide perovskites without halide segregation. *Current Opinion in Electrochemistry*, (2018) DOI: 10.1016/j.coelec.2018.09.007 (Chosen paper as the cover figure of the volume).
- A. F. Gualdrón-Reyes, A. M. Meléndez, J. Tirado, M. A. Mejía-Escobar, F. Jaramillo, M. E. Niño-Gómez, Hidden energy levels? Carrier transport ability into CdS/CdS<sub>1-x</sub>Se<sub>x</sub> quantum dot solar cells affected by Cd-Cd states formation. *Nanoscale*, NR-ART-08-2018-007073, Just accepted.
- A. F. Gualdrón-Reyes, S. J. Yoon, E. M. Barea, S. Agouram, V. Muñoz-Sanjose, A. M. Meléndez, M. E. Niño-Gómez, I. Mora-Seró, Direct measurement of crystal size for phase segregation in CsPbBr<sub>3-x</sub>I<sub>x</sub> mixed halide perovskites. *ACS Energy Letters*, nz-2018-02207k, under corrections.
- M. I. Carreño-Lizcano, <u>A. F. Gualdrón-Reyes</u>, V. Rodríguez-González, A. Pedraza-Avella, M. E. Niño-Gómez, Photoelectrocatalytic phenol oxidation employing nitrogen doped TiO<sub>2</sub>-rGO films as photoanodes. *Catalysis Today,* under revision.
- 11. <u>A. F. Gualdrón-Reyes</u>, J. S. Rios-Niño, A. M. Meléndez, M. A. Mejía-Escobar, F. Jaramillo, M. E. Niño-Gómez, An alternative to enhance band structure mismatch into Bi<sub>2</sub>S<sub>3</sub> based solar cells: Mn-doped CdS quantum dots type bridges. *RSC Advances*, under revision.

 D. Cardenas-Morcoso, <u>A. F. Gualdrón-Reyes</u>, A. B. Ferreira-Vitoreti, M. García-Tecedor, S. J. Yoon, M. S. de la Fuente, I. Mora-Seró, S. Gimenez, Photocatalytic and photoelectrochemical degradation of organic pollutants with all-inorganic metal halide perovskite quantum dots. *Nanoscale*, NR-ART-11-2018-009244, under revision.